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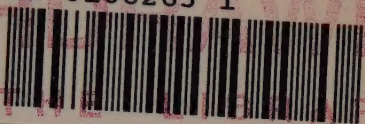
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100

ATOMIC STRUCTURE

ATOMIC STRUCTURE

AS MODIFIED BY
OXIDATION AND REDUCTION

BY

WILLIAM COLEBROOK REYNOLDS

D.Sc. (LOND.), F.I.C., A.R.C.S.

WITH DIAGRAMS AND A FOLDING TABLE



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PREFACE.

IN this small volume the results of a theoretical investigation of the structural changes which occur in atoms during the processes of oxidation and reduction are recorded. Many chemists realise that weighty problems lie behind these phenomena. As the well-known American chemist, Professor G. N. Lewis, has remarked, "In all chemistry there is no concept which is more fundamental than this one of oxidation and reduction." * Such considerations naturally make less appeal to Physicists and Mathematicians who have generally ignored them in developing structural systems.

The hypothesis that all the electrons situated at the same nuclear distance or level are necessarily retained with equal forces, is called in question. One can calculate the explosive charge necessary to blow open a safe—neglecting the consideration that a turn of the key may effect the same purpose.

It is hoped that sufficient evidence has been brought forward in these pages to focus scientific attention on another aspect of the subject, namely, the association of the electrons in groups which are symmetrically distributed around the nuclei of atoms.

It is, however, the presence of potential valence electrons—never exceeding six in number—which is the special

* "Valence," p. 69.

feature of atomic structure to which attention is particularly directed below.

Recognition of the part played by these potential valence electrons leads at once to a modified conception of the Periodic Classification of the elements, and to definite ideas concerning the structure of the "Rare Earth" and "Transition" elements.

In a chapter devoted to organic chemistry some important new considerations are raised that affect some of our fundamental conceptions in this field.

The mechanism of electrical conductivity in Graphite and the metals, and that of magnetism in Iron and Heusler's alloys is discussed from the new standpoint.

As the study of the oxidation and reduction phenomena associated with the molecules of chromophores indicates that certain movements characterise the interplay between these and radiation, three chapters have been devoted to the development of this subject, including one on the general relationships of ether and matter, in which the chemistry of the ether is investigated, and evidence pointing to the existence of two new "ethereal elements" is reviewed. Interesting deductions concerning the nature of some of the most important phenomena in physical optics, as viewed from a fresh standpoint, are outlined.

The size of the volume has permitted but scant reference to the publications of other workers and writers on the subject, but the timely appearance of Mr. Douglas Clark's "Basis of Modern Atomic Theory" has made the compilation of bibliographies on this subject unnecessary.

CONTENTS.

CHAPTER I.

A VIEW OF ATOMIC STRUCTURE AND THE PERIODIC CLASSIFICATION.

	PAGE
Introduction—The three classes of electrons—The valence electrons—The potential valence electrons—The radial pairs and quartets—The periodic sub-groups—Table of electron distribution of the elements—The three sections of the periodic classification—The valence section—The potential valence section—The rare earth section	I

CHAPTER II.

ATOMIC ASSOCIATION.

The factors concerned with atomic association—Electrostatic forces—Pictorial representation—Magnetic forces—The Faraday phenomena—Crystal formation—Change of state—The factors concerned with symmetry—Centrifugal force—Variable symmetry—Three notable volatile compounds—Dissociation—Atomic volume—Steric hindrance—Stability of optical isomers—Complex compounds—Ice—Ammonium salts—Silicofluorides—Platinichlorides—Quartz—Double iodides—Ferrocyanides—Ionic condensations—Catalysis	16
---	----

CHAPTER III.

THE OXIDATION AND REDUCTION OF TYPICAL INORGANIC SUBSTANCES.

Types of oxidation—Terminology and definitions—Eastman's views—The two kinds of oxidation or activation, basic and acidic—Sulphur—Chlorine—Phosphorus—The Platinum, Palladium, and Iron families—The dual rôles of chromium and manganese—Gold—Double pairs or quartets?—Nuclear distance and stability	33
---	----

CHAPTER IV.

THE OXIDATION AND REDUCTION OF ORGANIC SUBSTANCES.

Comparison of the states of manganese with those of carbon and nitrogen—The difficulties of existing nomenclature—The structure of the simpler compounds of carbon and nitrogen—Double and triple bonds—Hydrogen as a connecting-link—The magnetic fields of unsaturated bodies—Tautomeric changes in unsaturated bodies—Shifting bonds—The latent valence of

aldehydes and ketones—Combustion—Acids—Quinones— Cyclic compounds—Para changes—Condensed cyclic com- pounds	43
---	----

CHAPTER V.

THE NATURE OF CHROMOPHORES.

The migrations of unstable potential valence electrons—Types of chromophores—Azo compounds—Nitrobenzene—Nitrogen peroxide—Quinones—Alizarin—Permanganates—Keto-enolic bodies—Acridine—Triphenylmethyl—Rosaniline—Indigo —Coloured cations—The rare earths—The halogens	57
--	----

CHAPTER VI.

THE EMISSION AND ABSORPTION OF RADIATION.

An oscillating electron theory—High temperature ionisation—Col- lapsible shells—The Balmer relation—Line absorption—Band absorption and emission—Moving shells—Electron migration —Body and surface colour—Anomalous dispersion—Fluor- escence—Phosphorescence—X-rays—Kossel's theory—Shells and their frequencies—The significance of Ruthenium and Osmium—Barkla's K, L, M, N, and O series	68
---	----

CHAPTER VII.

THE STRUCTURE OF SOLID CONDUCTORS AND MAGNETS.

The allotropic varieties of carbon—Diamond—Graphite—The mechanism of conductivity—Opacity—Reduction—The con- ductivity of selenium—Conduction and chromophoric proper- ties—Temperature and conduction—Insulators—Metallic re- flection—Shell reorientation—The alkali metals—Metallic ions —The ferromagnetism of iron—Metallic structure—Heusler's alloys—The structure of strained metals	81
--	----

CHAPTER VIII.

ELECTRONS, PROTONS, AND ETHER.

Conflicting views regarding the ether—The assumed homogeneity of the ether—Transverse vibrations—The two constituents of the ether—The nature of electrostatic force—Slow synthetic forces—The hydrogen nucleus and protons—Mass varies with time—Mass and velocity—Gravitation—Newton's view of the ether probably correct—Magnetism—Faraday's tubes of force —Spinning electrons and protons—The magnetic fields in atoms—Induced currents—Diamagnetism—The nature of radiation—Radiation in space a magnetic phenomenon—A mode of polarisation—The two modes of reflection—Non-pola- rising surfaces—Refraction—Dispersion—Photoelectric effects —Newton's corpuscles—Relativity—Effect of ether currents on the velocity of light—Gravitational aberration	99
INDEX	125

CHAPTER I.

A VIEW OF ATOMIC STRUCTURE AND THE PERIODIC CLASSIFICATION.

Introduction.

CHEMISTS have become accustomed to the idea that when one substance is oxidised another is reduced. When, for instance, ferrous salts are oxidised to ferric, corresponding quantitative changes in permanganates or bichromates are observed. They express the reactions by equations which tell part of the story—the energy side constitutes a second phase.

When bromine is taken up by unsaturated organic bodies, is there any collateral change comparable with that which occurs when bromine combines with ferrous bromide? Is the addition of hydrogen instead of bromine, to the unsaturated body, one of oxidation or reduction? Are all oxidation processes comparable? In what sense are alcohols and phenols oxidation products of the corresponding hydrocarbons? Dyes and colouring matters present many interesting and important problems concerning oxidation and reduction, as the existence of leuco bodies and colourless isomers remind us. Is the possession of colour evidence that internal molecular change is continually proceeding, involving the alternate oxidation and reduction of certain atoms of the molecule? Do the different allotropic forms of an element belong to the same state of reduction?

A few years ago such considerations would have seemed of but slight importance, but to-day chemists are paying attention to yet a third phase of such phenomena, and are

trying to interpret chemical change in terms of electron re-distribution and movements. It is this phase of oxidation and reduction that is emphasised here, in the confident belief that we shall eventually fashion the key that will unlock the doors of these mysterious compartments.

We shall attempt to demonstrate that the accuracy of our interpretation of the Periodic Table and many of the most fundamental chemical and physical phenomena, depends on the correct answer to the above and similar problems. Theory and practice are inextricably mixed up. Our plans for building up structures, such as dyes, are to a considerable extent dependent on our theoretical conceptions regarding the nature of chromophores and other complexes.

Electron Classification.

The existence of the Rutherford atom with its central positive charge, surrounded by extranuclear electrons, in number equal to the figure indicated by Moseley's rule, is taken for granted in these pages, which are merely concerned with the distribution and functions of these constituents of the elements.

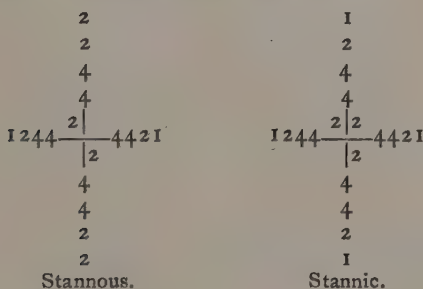
The present spectroscopic classification of these electrons is unsuitable for chemical discussion, and it is probable that it will undergo drastic modification before long. It is the physical counterpart of the artificial Linnæan classification in botany, and, like the latter, must ultimately for most purposes be discarded in favour of a natural system, when the science is sufficiently developed. For the present purpose, therefore, a purely chemical arrangement has been adopted. The simple explanation this furnishes of the structure of the Rare Earth and the transition elements, and the phenomena of oxidation and reduction in the latter, justifies its adoption.

The electrons appear to fall naturally into three classes—one or more of which may be absent. Not, of course, that electrons differ from one another, but their functions vary with their position, or rather centres of rotation, etc. Arranged in the order of their chemical activity these are :—

- I. The valence electrons.
- II. The potential valence electrons.
- III. The radial quartets and pairs.

The consideration of the orbital movements of these electrons and their magnetic and electrostatic fields is deferred to later chapters. At present the majority may be regarded as rotating in pairs or quartets about a few symmetrically placed centres *outside* the nucleus. Electrons moving in planetary fashion around central nuclei, or in cassinian curves about two, have yet to justify chemical consideration.

A method of exhibiting these different classes in plane diagrams is shown in Diagram I., where those present in tin, atomic number 50, in stannous and stannic chlorides are represented (dissected from the halogen)—



The number of *potential valence electrons* is for convenience depicted nearest the centre, although they are not all situated nearer the nucleus than the radial electrons. In stannic chloride the number is given as 2, 2, 2 rather than 6 as it is probable that the nuclear distances of the six are not the same (see Chapter VI.).

The *radial quartets and pairs* are shown outside the arms of the cross, and outside these are the *valence* electrons. For simplicity they are shown in alignment with the radial electrons, but this is not necessarily their position in space, in fact, as we shall see later, they are known to be distributed otherwise in such compounds as CaCO_3 , NaNO_3 , PCl_5 , and SiO_2 .

In the present chapter it will be convenient (to briefly summarise the functions of the electrons forming these classes, and then draw attention to certain important features of the periodic classification of the elements, leaving consideration of details to later chapters.

Valence Electrons.

The valence electrons are farthest from the nucleus. Their number varies from 0 to 7 in different atoms. The elements of any one of the eight groups of the valence section of the periodic classification have, or may have, the same number of valence electrons.

Valence electrons are associated in pairs at ordinary temperatures, single valence electrons being unknown except during the moment of chemical change.

Valence pairs are formed in two ways :—

I. The atom combines with one or more of those of the same or a different element, an electron from the valence system of each forming the pair or “bond” which “unites,” and is common to the valence system of each. The axis of rotation of the pair is probably the line joining the two nuclei.

II. When an atom has four or more valence electrons the latter may unite to form one or more pairs. Such pairs may remain unassociated (*latent* valence pairs), or they may associate with the valence system of other atoms such as oxygen (*active* valence pairs).

When several valence pairs are associated with a nucleus, these are distributed symmetrically around it like the angles of simple geometrical forms such as the tetrahedron, square, and octahedron. In a few cases five pairs occur.

The disposition of the valence pairs around an atom frequently varies with the nature and number of the surrounding atoms in the compound, and by means of oxidation and reduction the number of valence electrons can be increased or diminished by the transference of one or more from or to the potential valence system.

The Potential Valence Electrons.

These electrons play no direct part in chemical reactions. It is only after they have been transferred to outer valence positions by the operations of oxidation or reduction that they display chemical activity.

The potential valence electrons never exceed six in number. Among the Rare Earth and transition elements there is repeated evidence that this limiting condition is of fundamental importance in atomic architecture. Possibly this is due to their being arranged about three axes at right angles, although two of them appear to be more difficult to displace than the others, and rarely change their position except in the case of the elements of the first period. This is the only class in which odd electrons occur in stable atoms.

Most of the elements of Groups 0 to 3 form one series of salts only—copper, gold, mercury, and thallium being exceptional—hence the number of potential valence electrons generally remains constant in the first half of each period. On the other hand, the number is variable in the elements of the Rare Earths, the transition families, and Groups 4 to 7.

In the case of those metals which form more than one series of salts, oxidation from the “ous” to the “ic” variety involves the transfer of one or more valence electrons to the potential valence system.

In addition to this basic type of “oxidation” there is an acidic type in which *the direction of electron transfer is reversed*, and still a third in which no transfer occurs.

Permanganates, sulphates, carbonates, nitrates, etc., are acidic oxidation products in which the minimum number of potential valence electrons are present.

In general that compound of an element containing the highest proportion of hydrogen is the least acidic, and has the largest number of potential valence electrons, and the acid containing the largest proportion of oxygen has the least number of potential valence electrons. The latter remain invariable in the inert gases, alkali metals, and halogens.

The variation of the nuclear distance of valence electrons during chemical change was until recently a purely theoretical deduction, but S. K. Allison (J. Washington Acad. Sci., 1926 ; 16, 7), pursuing a line opened up by A. E. Lindh, has demonstrated that the levels of certain electrons in silicon, phosphorus, and sulphur, as determined by X-ray analysis, varies with their state of oxidation. These results are very significant, and the extension of such work to the case of "ous" and "ic" salts, may well prove of fundamental importance in atomic theory.

The Radial Pairs.

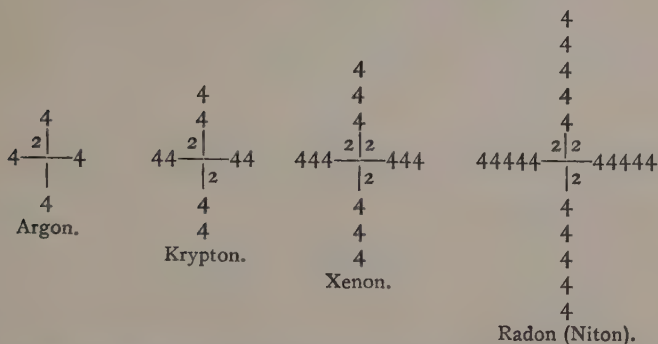
When more than four valence electrons are present in an atom, there is a marked tendency, as has been already pointed out, for the latter to form one or more latent pairs.

When eight outer electrons are present, these form four pairs, and further valence electrons occupy orbits outside these radial pairs.

The radial pairs but seldom take part directly in chemical reactions which almost exclusively concern the valence electrons. It is possible, however, that they play an active part in forming the complexes present in certain metallic crystals, for it is noticeable that the elements which are employed in metallurgical operations, copper, aluminium, silver, tin, gold, zinc, magnesium, cadmium, lead, iron, cobalt, nickel, and platinum all contain either four radial pairs or several latent valence pairs. In the case of the silicates it is probable that two of these pairs are concerned with their tendency to form complex molecules, and magnesium in the Grignard reaction betrays a similar tendency.

The Radial Quartets.

The fact that the radial electrons of the inert gases from argon onwards increase each time by four quartets is very significant—



If the innermost radial shells of complex atoms consisted of pairs, there should be inert gases in Group o immediately preceding copper, silver, and gold.

It appears, therefore, that when two pairs revolve about coaxial orbits, these coalesce into a quartet.

The four quartets are probably arranged about four axes radiating symmetrically from the nucleus; the four electrons of each quartet are symmetrically distributed round their common orbit which lies in the plane at right angles to the axis, each electron following a spiral path around the orbit.

The radial quartets, except in the case of cerium, play no direct part in chemical reactions.

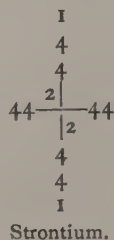
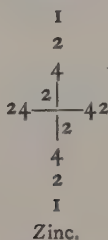
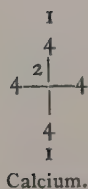
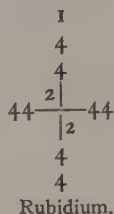
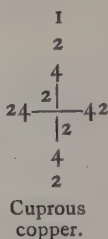
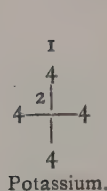
The Rare Earths excepted, the four radial groups of the elements are similar in composition.

The addition of eight further electrons outside radial quartets again leads to the formation of four radial pairs beyond which the valence electrons are situated.

The Periodic Sub-Groups.

Whilst the radial system of the elements of the first half of each long period consists of quartets, those of the second half have in addition four radial pairs outside the quartets, and it is the presence of the latter which distinguishes the members of such sub-groups as zinc, cadmium, and mercury, from the allied quartet group calcium, strontium, and barium, also copper, silver, and gold from the quartet alkalis potassium, rubidium, and cæsium.

The Sub-Groups—A Comparison.



The distribution of the electrons in the elements, dissected from typical compounds, in terms of the above classes, is displayed in the accompanying table. A glance at Diagram I. will explain the convention adopted in displaying this distribution in plane diagrams.

It is, of course, understood that the distribution as between the valence and potential valence classes is subject to mutual rearrangement according to the state of oxidation of the compound under consideration.

TABLE SHOWING THE DISTRIBUTION OF THE ELECTRONS IN TYPICAL COMPOUNDS OF ALL THE ELEMENTS.

Atomic Number.	Symbol.	Valence Electrons.	Potential Valence Electrons.	Radial Pairs.	Radial Quartets.
1	H	1	—	—	—
2	He	—	2	—	—
3	Li	1	2	—	—
4	Be	2	2	—	—
5	B	3	2	—	—
6	C	4	2	—	—
7	N	5	2	—	—

Atomic Number.	Symbol.	Valence Electrons.	Potential Valence Electrons.	Radial Pairs.	Radial Quartets.
8	O	6	2	—	—
9	F	7	2	—	—
10	Ne	—	2	4	—
11	Na	1	2	4	—
12	Mg	2	2	4	—
13	Al	3	2	4	—
14	Si	4	2	4	—
15	P	5	2	4	—
16	S	6	2	4	—
17	Cl	7	2	4	—
18	A	—	2	—	4
19	K	1	2	—	4
20	Ca	2	2	—	4
21	Sc	3	2	—	4
22	Ti	4	2	—	4
23	V	5	2	—	4
24	Cr (ous)	6	2	—	4
25	Mn (ous)	6	3	—	4
26	Fe (ous)	6	4	—	4
27	Co (ous)	6	5	—	4
28	Ni (ous)	6	6	—	4
29	Cu (ous)	1	4	4	4
30	Zn	2	4	4	4
31	Ga	3	4	4	4
32	Ge	4	4	4	4
33	As	5	4	4	4
34	Se	6	4	4	4
35	Br	7	4	4	4
36	Kr	—	4	—	4 × 2
37	Rb	1	4	—	4 × 2
38	Sr	2	4	—	4 × 2
39	Y	3	4	—	4 × 2
40	Zr	4	4	—	4 × 2
41	Cb	5	4	—	4 × 2
42	Mo	6	4	—	4 × 2
43	Ma	7	4	—	4 × 2
44	Ru	4	4	2	4 × 2
45	Rh	4	5	2	4 × 2
46	Pd	4	6	2	4 × 2
47	Ag	1	6	4	4 × 2
48	Cd	2	6	4	4 × 2
49	In	3	6	4	4 × 2
50	Sn	4	6	4	4 × 2
51	Sb	5	6	4	4 × 2

TABLE SHOWING DISTRIBUTION OF ELECTRONS—(cont.).

Atomic Number.	Symbol.	Valence Electrons.	Potential Valence Electrons.	Radial Pairs.	Radial Quartets.
52	Te	6	6	4	4×2
53	I	7	6	4	4×2
54	Xe	—	6	—	4×3
55	Cs	1	6	—	4×3
56	Ba	2	6	—	4×3
57	La	3	6	—	4×3
58	Ce (ic)	4	6	—	4×3
58	Ce (ous)	3	3	—	$4 \times 3 + 1$
59	Pr	3	4	—	$4 \times 3 + 1$
60	Nd	3	5	—	$4 \times 3 + 1$
61	Il	3	6	—	$4 \times 3 + 1$
62	Sm	3	3	—	$4 \times 3 + 2$
63	Eu	3	4	—	$4 \times 3 + 2$
64	Gd	3	5	—	$4 \times 3 + 2$
65	Tb	3	6	—	$4 \times 3 + 2$
66	Dy	3	3	—	$4 \times 3 + 3$
67	Ho	3	4	—	$4 \times 3 + 3$
68	Er	3	5	—	$4 \times 3 + 3$
69	Tm	3	6	—	$4 \times 3 + 3$
70	Yb	3	3	—	4×4
71	Lu	3	4	—	4×4
72	Hf	4	4	—	4×4
73	Ta	5	4	—	4×4
74	W	6	4	—	4×4
75	~~Re~~	7	4	—	4×4
76	Os	4	4	2	4×4
77	Ir	4	5	2	4×4
78	Pt	4	6	2	4×4
79	Au (ous)	1	6	4	4×4
80	Hg (ic)	2	6	4	4×4
81	Tl (ic)	3	6	4	4×4
82	Pb	4	6	4	4×4
83	Bi	5	6	4	4×4
84	Po	6	6	4	4×4
85	—	7	6	4	4×4
86	Rn	—	6	—	4×5
87	—	1	6	—	4×5
88	Ra	2	6	—	4×5
89	~~Ac~~	3	6	—	4×5
90	Th	4	6	—	4×5
91	Pa	5	6	—	4×5
92	Ur	6	6	—	4×5

The Periodic System.

The properties of the elements depend, of course, on the distribution of their electrons.

As the number of the extranuclear electrons, *i.e.* the atomic number, increases, the extra electrons pass into the valence system for a period, after which they tend to pass into the potential valence system for a further period, and so on alternately. As these two systems are themselves variable, the periods are not sharply defined—the same element may belong to either section according to its state of oxidation. When these systems contain their maximum number of electrons, *i.e.* 7 and 6 respectively, further additions take up positions outside the earlier groupings which then become the radial pairs or radial quartets.

When the Rare Earth elements are reached at cerium, the third type of development is seen, and short periods occur in which the number of potential valence electrons regularly increase until six are present when four are transformed in turn into radial quartets as described below. This process goes on until yttrium is reached, after which the earlier type of development is again resumed.

Hence there are three sections of the periodic system.

- I. The main section. In this the characteristic variable is the valence system.
- II. The transition sections. Here the characteristic variable is the potential valence system.
- III. The Rare Earth section. The characteristic variables in this case are the potential valence and radial systems.

The Valence Section.

In Table I. the electron distribution of the valence section of the periodic system is set out.

It must be borne in mind in considering Groups 4 to 7 that the number of valence and potential valence electrons shown are to some extent interchangeable according to the state of oxidation. Arrows indicate the periodic discontinuities.

The Potential Valence Section.

In the potential valence section the distribution is displayed in diagrams as on page 3. These facilitate comparisons between the structures of different salts, such as the ferrous and ferric. It will be noted that the type of development ceases as soon as six potential valence electrons are present, and it is noteworthy that nickelic salts, where there would be seven, are unknown.

Chromium and manganese belong to both sections of the periodic system. In their acidic combinations—the chromates, manganates, and permanganates—these elements belong to the valence section. In their basic rôles they may be regarded as the first members of the iron family.

The elements Mn, Fe, Co, and Ni all form double carbonates of the composition $MCO_3 \cdot K_2CO_3 \cdot 4H_2O$.

Cr, Mn, Fe, and Co all form complex cyanides of the types $K_4M(CN)_6$ and $K_3M(CN)_6$, and all form salts of the type MCl_2 .

On the other hand, elements 43 and 75, the discovery of which was announced some time ago but particulars of

PERIODIC TABLE—POTENTIAL VALENCE SECTION.

IRON FAMILY.

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"ous" salts	Cr 24	Mn 25	Fe 26	Co 27	Ni 28
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"ic" salts					

PALLADIUM FAMILY.

"ous" salts	$\begin{array}{c} 2 \\ 4 \times 2 \\ 1.2.4 \times 2 \frac{2}{1} 4 \times 2.2.1 \\ \\ 4 \times 2 \\ 2 \end{array}$ Ru 44	$\begin{array}{c} 2 \\ 4 \times 2 \\ 1.2.4 \times 2 \frac{2}{1} 4 \times 2.2.1 \\ \\ 4 \times 2 \\ 2 \end{array}$ Rh 45	$\begin{array}{c} 2 \\ 4 \times 2 \\ 1.2.4 \times 2 \frac{2}{2} 4 \times 2.2.1 \\ \\ 4 \times 2 \\ 2 \end{array}$ Pd 46
	$\begin{array}{c} I \\ 4 \times 2 \\ 1.2.4 \times 2 \frac{2}{2} 4 \times 2.2.1 \\ \\ 4 \times 2 \\ I \end{array}$	$\begin{array}{c} I \\ 4 \times 2 \\ 1.2.4 \times 2 \frac{2}{2} 4 \times 2.2.1 \\ \\ 4 \times 2 \\ I \end{array}$	$\begin{array}{c} I \\ 4 \times 2 \\ 1.2.4 \times 2 \frac{2}{2} 4 \times 2.2.1 \\ \\ 4 \times 2 \\ I \end{array}$

PLATINUM FAMILY.

"ous" salts	$\begin{array}{c} 2 \\ 4 \times 4 \\ 1.2.4 \times 4 \frac{2}{1} 4 \times 4.2.1 \\ \\ 4 \times 4 \\ 2 \end{array}$ Os 76	$\begin{array}{c} 2 \\ 4 \times 4 \\ 1.2.4 \times 4 \frac{2}{1} 4 \times 4.2.1 \\ \\ 4 \times 4 \\ 2 \end{array}$ Ir 77	$\begin{array}{c} 2 \\ 4 \times 4 \\ 1.2.4 \times 4 \frac{2}{2} 4 \times 4.2.1 \\ \\ 4 \times 4 \\ 2 \end{array}$ Pt 78
	$\begin{array}{c} I \\ 4 \times 4 \\ 1.2.4 \times 4 \frac{2}{2} 4 \times 4.2.1 \\ \\ 4 \times 4 \\ I \end{array}$	$\begin{array}{c} I \\ 4 \times 4 \\ 1.2.4 \times 4 \frac{2}{2} 4 \times 4.2.1 \\ \\ 4 \times 4 \\ I \end{array}$	$\begin{array}{c} I \\ 4 \times 4 \\ 1.2.4 \times 4 \frac{2}{2} 4 \times 4.2.1 \\ \\ 4 \times 4 \\ I \end{array}$

which are still awaited, cannot be members of the palladium and platinum families in the sense of forming two chlorides of the type MCl_2 and MCl_4 both structurally analogous to those of ruthenium and osmium.

In this section some of the external pairs may be regarded

as latent valence pairs or as radial pairs—the two classes mutually converge.

The Rare Earths.

The structure of this interesting section is relatively simple. On reference to the table on page 9 it will be noted that the elements preceding cerium, already possess six inner electrons. Hence the method of development seen in the iron and palladium families cannot be followed here, *i.e.* by additions to the potential valence system, accompanied by the formation of two more elements than the valence section of the periodic system can accommodate, followed by the appearance of two extra potential electrons in the succeeding periods. In reality the reverse is the case; there are two elements less than the valence section requires, instead of two more, and the succeeding period contains two fewer potential valence electrons.

In the previous periods the additions to the radial system occur in sudden jumps, *all four radial groups increasing simultaneously*. In the Rare Earths the additions are made to the four radial groups *one at a time*, hence there are four families in the Rare Earths.

Cerium forms two series of salts, CeCl_4 and CeCl_3 . The former belongs to the valence section, and the latter to the new one.

In the new system the valence electrons are retained, and additions are made to the potential valence system until six are present, when an addition of four is made to each radial group in turn. Finally at lutecium the first system of growth is resumed.

It may be noted that the four families of the Rare Earths that are envisaged by these theoretical considerations are practically identical with the four groupings that have been adopted, on chemical and physical grounds, by Levy in his volume on the "Rare Earths." The chief difference between the two concerns the position of samarium, which Levy has placed in the cerium group, which closes here with Prof. Hopkins' recently announced illinium. Levy, however, remarks in the text that samarium appears to lie between neodymium and the terbium earths.

A VIEW OF ATOMIC STRUCTURE

PERIODIC TABLE—RARE EARTH SECTION.

15

$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid \\ 1.3 \times 4 \frac{\quad}{1} 3 \times 4.1 \\ 4 \times 4 \\ \text{Ce (ous)} \end{array}$ 58	$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid \\ 1.3 \times 4 \frac{\quad}{2} 3 \times 4.1 \\ 4 \times 4 \\ \text{Pr} \end{array}$ 59	$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid 1 \\ 1.3 \times 4 \frac{\quad}{2} 3 \times 4.1 \\ 4 \times 4 \\ \text{Nd} \end{array}$ 60	$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid 2 \\ 1.3 \times 4 \frac{\quad}{2} 3 \times 4.1 \\ 4 \times 4 \\ \text{II} \end{array}$ 61
$\begin{array}{c} \text{I} \\ 4 \times 4 \\ 2 \mid \\ 1.3 \times 4 \frac{\quad}{1} 3 \times 4.1 \\ 4 \times 4 \\ \text{Sm} \end{array}$ 62	$\begin{array}{c} \text{I} \\ 4 \times 4 \\ 2 \mid \\ 1.3 \times 4 \frac{\quad}{2} 3 \times 4.1 \\ 4 \times 4 \\ \text{Eu} \end{array}$ 63	$\begin{array}{c} \text{I} \\ 4 \times 4 \\ 2 \mid 1 \\ 1.3 \times 4 \frac{\quad}{2} 3 \times 4.1 \\ 4 \times 4 \\ \text{Gd} \end{array}$ 64	$\begin{array}{c} \text{I} \\ 4 \times 4 \\ 2 \mid 2 \\ 1.3 \times 4 \frac{\quad}{2} 3 \times 4.1 \\ 4 \times 4 \\ \text{Tb} \end{array}$ 65
$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid \\ 1.4 \times 4 \frac{\quad}{1} 4 \times 4.1 \\ 4 \times 4 \\ \text{Dy} \end{array}$ 66	$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid \\ 1.4 \times 4 \frac{\quad}{2} 4 \times 4.1 \\ 4 \times 4 \\ \text{Ho} \end{array}$ 67	$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid 1 \\ 1.4 \times 4 \frac{\quad}{2} 4 \times 4.1 \\ 4 \times 4 \\ \text{Er} \end{array}$ 68	$\begin{array}{c} \text{I} \\ 3 \times 4 \\ 2 \mid 2 \\ 1.4 \times 4 \frac{\quad}{2} 4 \times 4.1 \\ 4 \times 4 \\ \text{Tm} \end{array}$ 69
$\begin{array}{c} \text{I} \\ 4 \times 4 \\ 2 \mid \\ 1.4 \times 4 \frac{\quad}{1} 4 \times 4.1 \\ 4 \times 4 \\ \text{Yb} \end{array}$ 70	$\begin{array}{c} \text{I} \\ 4 \times 4 \\ 2 \mid \\ 1.4 \times 4 \frac{\quad}{2} 4 \times 4.1 \\ 4 \times 4 \\ \text{Lu} \end{array}$ 71		

CHAPTER II.

ATOMIC ASSOCIATION.

ALL atoms display some tendency to unite with others, for even the inert gases can be liquefied or solidified. There is no sharp division between physical and chemical association; molecules of water vapour may associate superficially with cupric oxide, asbestos, charcoal, ice, glycerine, calcium chloride, or anhydrous sodium carbonate, and we may refer to the phenomena as adsorption, change of state, deliquescence or water of crystallisation, but the mechanism is possibly much the same in each case, the hydrogen nucleus being balanced between two paired electron shells, one on the oxygen atom and another on the condensing surface. On the other hand, when they condense on an anhydride like phosphorus pentoxide the water molecules are split up, and the oxygen is directly associated with the phosphorus through pair shells. No one, perhaps, would deny that the latter was a chemical reaction, but it is impossible to frame a definition of chemical force which would apply to some of the above phenomena and exclude the others.

In the present chapter some of the factors which appear to play an important part when atoms associate with others to form complex systems are considered, as a preliminary to the discussion of problems concerning oxidation and reduction which are dealt with in the following chapters.

The factors are treated under the following headings: *Electrostatic Force, Magnetic Force, Symmetry and Centrifugal Force, and Atomic Volume.*

Gravity, which is referred to in Chapter VIII., is believed to play only a minor part in the chemical union of atoms.

Electrostatic Force.

The paired electron shell forms the "bond" or mechanism of union between atomic nuclei in all cases of stable chemical union, but for structural purposes it is necessary to distinguish between two types of shells.

I. Pairs made up of electrons drawn from the valence system of two atoms or *heterovalent pairs* :—

examples H_2O CH_4 NH_3 LiF .

II. Pairs formed of electrons drawn from the valence system of one of the atoms only, or *homovalent pairs* :—

examples CaO SiO_2 RuO_4 .

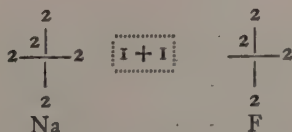
In compounds containing several atoms some may be united by the first and others by the second type of pair :—

examples KClO_4 NH_4Cl HBF_4 .

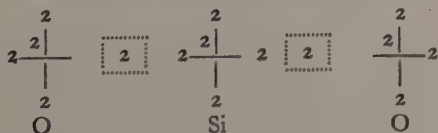
The so-called electrovalent compounds constitute an extreme phase of the first type, alcohol, water, and the alkalis on the one hand, and water, phenol, and various acids on the other forming two convergent series, in the aqueous solutions of which almost every degree of electrolytic dissociation may be observed.

Graphic Representation.

When it is necessary to indicate the electron structure of a compound, the plane diagrams of Chapter I. may be employed. For example, on dissecting sodium fluoride it becomes



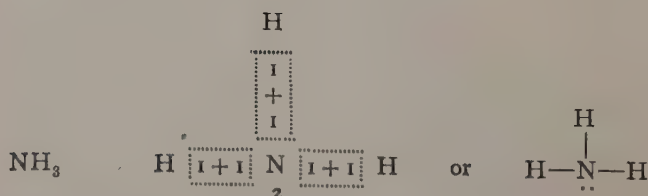
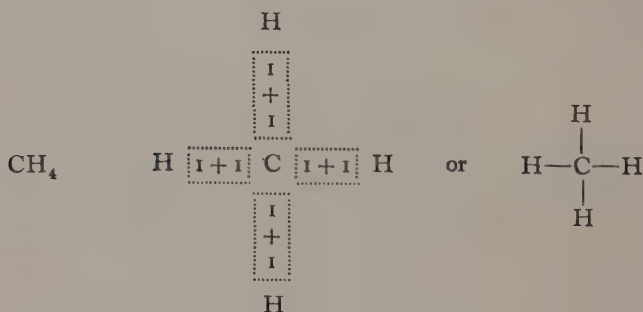
Silicon dioxide may be similarly represented as



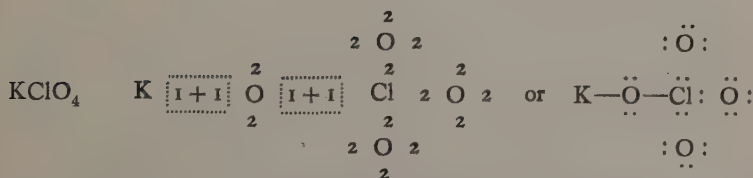
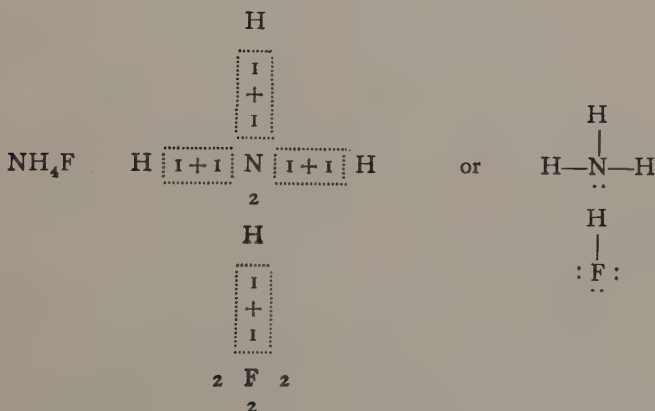
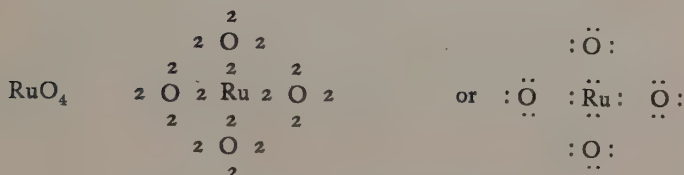
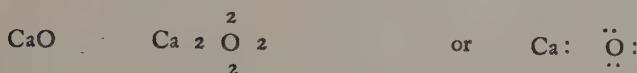
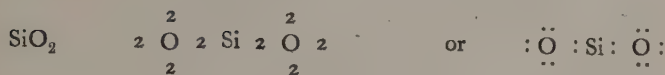
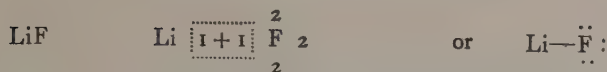
In the former the single valence electron of the sodium completes the four fluorine pairs, and in the latter the fourth pair of each oxygen atom is drawn entirely from the four valence electrons of the silicon.

For many purposes, however, only the valence electrons need be shown. By adopting a convention, the time-honoured bonds that have played such a prominent part in structural chemistry can be employed for the purpose, and this is all the more desirable as they have proved indispensable in the development of organic chemistry.

If a light bond is used to join two atoms A—B connected by a paired shell of the first or heterovalent type, and two dots near to A: B to represent a pair formed from the valence electrons of A only (a homovalent pair),* the valence structure of the atoms in compounds can be simply represented by bonds. Taking the examples quoted above these can be represented as follows :—



* An arrow directed towards the atom furnishing the homovalent can be employed alternatively.



The nature of electrostatic force is discussed in Chapter VIII.

Magnetic Force.

Every molecule possesses a magnetic field. This follows at once from the results of Faraday's researches during 1845-6. Among other facts he demonstrated that polarised light, when passed through any liquid in a magnetic field, had its plane of polarisation rotated in proportion to the strength of the field.

This phase of the subject has since been carefully examined by Sir Wm. Perkin, but it is remarkable how little is known as to the effect of magnetic fields on the course of chemical reactions and molecular kinetics. It is probable that results of the greatest theoretical, and perhaps even industrial importance, will reward future workers in this field.

Electron pairs and quartets, which form the external structural units of atoms, revolving in circular or elliptical orbits, constitute magnetic shells. Under ordinary circumstances the atomic magnetic fields are masked at macroscopic distances because the electron shells are so grouped around nuclei that their external fields are greatly reduced.

In like manner atomic magnetic fields are again reduced when atoms associate to form complex molecules, and these molecular fields are still further diminished by the character of the orientation of the molecules in crystals. Unless external fields are superimposed, atomic association proceeds in such a manner that local electrostatic and magnetic fields cancel one another, and the external fields tend towards a minimum. The Faraday phenomenon indicates that the kinetic movements of molecules in gases and liquids normally prevent definite orientation, and it is only in the presence of external fields that polarised light reveals the fact that some similarity of magnetic alignment has been imposed on mobile molecules.

The properties of liquid crystals and films indicate that orientated association at times precedes definite crystallisation. At all material surfaces of separation, however, with the possible exception of metallic ones, the external layer consists of either hydrogen nuclei or electron magnetic shells, and

hence, although magnetic fields are negligible at macroscopic distances, strong local superficial magnetic fields at atomic distances (a few Angstrom units) must be present, and these doubtless are the dominant factor in "wetting," dissolution, crystal formation, catalysis, etc.

As a crude molecular analogy the following arrangement may be considered :—

Two similar irregular shaped boards, Fig. 1 A, are placed vertically over and near each other, one floating on water and the other suspended in a stirrup in the air above.

If magnets are placed in similar positions on each board, the latter will turn, and in the absence of external fields, they

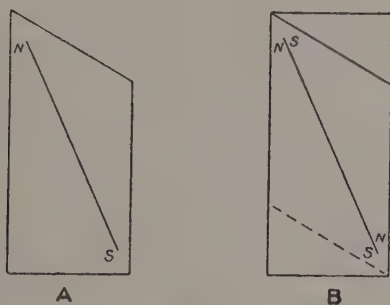


FIG. 1.

will take up positions as in Fig. 1 B, symmetrically placed "facets" being formed.

The constituents of crystal units are of course distributed in three dimensions, and their fields are complex, but magnetic forces analogous to the above probably determine the orientation of the molecules deposited on the faces of growing crystals, although both electrostatic and magnetic forces co-operate. In some cases electrolytic dissociation appears to persist in the solid state, and the electrostatic forces between the positive and negative ions give rise to structures such as those seen in sodium chloride for instance, where each chlorine and each sodium ion is surrounded symmetrically, octahedrally by six of the opposite variety. Certain oxides and sulphides show similar structures.

We can even get a glimpse of the kinetic side of the

picture when we consider the molecular lowering of the freezing-point of a solvent by a dissolved substance. A skeleton crystal of the solvent grows only when the number of suitably aligned molecules of solvent arriving exceeds the number departing, and the number arriving per unit time is diminished by the presence of dissolved molecules, independent of the character of the latter. Orientation requires time, and at lower temperatures a larger proportion of the more slowly moving molecules can orientate and attain suitable alignment, and the solvent crystal increases in spite of the presence of dissolved molecules.

Tetrahedral Bonds.

Although the four "bonds" or valence pairs are tetrahedrally grouped around the oxygen atoms in ice, and the carbon atoms in the diamond, nevertheless there is a different arrangement of the atoms in the crystals of these two substances as Sir Wm. Bragg has pointed out. If tetrahedral atomic models are placed vertically over each other, with one bond common to each, the three remaining bonds of either model appear to an observer placed above them to make angles of 120° with each other. In the case of ice (where hydrogen atoms are placed between the oxygen atoms) the bonds attached to the latter are directly over each other, but in the case of the diamond the one set of carbon bonds are exactly between those of the other. Hence we infer that the atomic magnetic forces direct the paired shells differently in the two cases.

Change of State.

The simultaneous existence of molecular forces of both repulsion and attraction, especially noticeable during liquefaction and vaporisation, has always presented theoretical difficulties. The phenomena may be concerned with magnetic reversals.

It may be that the polarity of one of the paired shells of colliding molecules is reversed during the change from the gaseous to the liquid state.

When one side of a floating coil conveying a current (such as a De la Rue battery) is approached by a similar magnetic pole, three phenomena are observable according to circumstances :—

- I. An approach of medium speed and short duration entails repulsion.
- II. A slow approach of longer duration ensures re-orientation of the shell and attraction.
- III. Very rapid approach leads to actual penetration.

When the kinetic movements and encounters * between gaseous molecules are considered I. may correspond to perfectly elastic encounters ; II. to the conditions on liquefaction where attraction prevails over repulsion ; III. to the conditions corresponding to high temperature ionisation.

Although astronomical analogies are not strictly comparable, the fact is worth recalling that two of Jupiter's nine satellites revolve in the opposite direction to the seven nearest the planet. We certainly cannot assume that all the magnetic shells around nuclei present the same pole towards the latter.

The magnetic fields within the atom and the part they play in maintaining an equilibrium between its constituent parts is discussed in Chapter VIII.

Atomic and Molecular Symmetry.

In recent times three distinct lines of investigation have drawn attention to the tendency of certain atoms or associations of atoms (radicals) to group themselves around a central atom in a *symmetrical* manner.

I. By the preparation of optically active compounds Sir William Pope and his assistants extended the tetrahedral hypothesis of Van't Hoff and Le Bel to atoms other than

* "I have concluded from some experiments of my own that the collision between two hard spherical balls is not an accurate representation of what takes place during the encounter of two molecules. A better representation of such an encounter will be obtained by supposing the molecules to act on one another in a more gradual manner, so that the action between them goes on for a finite time, during which the centres of the molecules first approach each other and then separate" (Clerk Maxwell, "On the Kinetic Theory of Gases").

carbon. At the present time this type of active molecule is associated with a dozen elements.

II. The researches of Werner and his disciples on complex compounds added greatly to our knowledge of chemistry in three dimensions, especially by the discovery of a new type of optically active molecule—one possessing octahedral symmetry. This is true of certain compounds of at least seven of the transition elements (potential valence section of the Periodic Table).

III. The wonderful development of X-ray methods of crystal analysis by Sir Wm. Bragg and others has extended the field of view to solid substances.

When we compare the results of these inquiries we note that when the number of atoms around a central one varies, it merely involves a change from one type of symmetry to another. For instance the tetrahedral symmetry of the optically active compounds of carbon and nitrogen is replaced in calcite and sodium nitrate by the symmetrical grouping of the three oxygen atoms around carbon and nitrogen respectively in the plane containing the central atom—the symmetry of the equilateral triangle.

As the result of his physical investigations at Zurich, Professor Henri has recently concluded that the symmetry of the distribution of the radicles around the carbon atom, in several organic compounds, varies according to the nature of the radicles.

The tetrahedral symmetry of the oxygen atoms around silicon in α - and β -quartz (Sir W. Bragg and R. E. Gibbs), beryl, olivine, and garnet (W. L. Bragg and J. West), and of the organic radicals in its optically active compounds (S. P. Kipping), changes to octahedral symmetry in the fluosilicates. The latter is probably true of sulphur in sulphur hexafluoride, whereas the oxygen atoms of sulphates and the organic radicals of optically active sulphur compounds exhibit tetrahedral symmetry around the sulphur.

Tin exhibits tetrahedral symmetry in SnI_4 and octahedral in $(\text{NH}_4)_2\text{SnCl}_6$.

Platinum and palladium, which exhibit octahedral symmetry in one class of compounds have been shown to possess

the plane symmetry of the corners of a square in another class. In basic beryllium acetate (described below) both tetrahedral and octahedral symmetry are seen in the same compound.

Metallic crystals showing either hexagonal or face centred cubic packing can be prepared in the case of cobalt and cerium.

Octahedral symmetry occurs in the case of ferro and ferricyanides. Unfortunately no information is available as yet regarding the symmetry of the penta-halogen compounds phosphorus, arsenic, antimony, stibium, and tungsten. When we inquire as to the reasons why several atoms should be symmetrically disposed about another, we note that the phenomenon probably depends on several factors :—

I. Electrostatic force tends to spread the valence electrons of the central atom apart until the pairs are equidistant from each other.

II. Magnetic force (referred to above).

III. The surrounding atoms or radicles may in some cases be forced apart because there is barely room for all of them around the central atom.

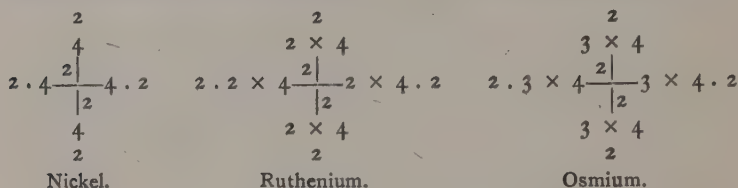
IV. Centrifugal force. It is probable that the statical consideration of molecular structure has hitherto received undue attention. The molecules of gases and liquids are dynamic units, and they are subject to centrifugal force, under which unsymmetrical structures tend to separate or dissociate.

The rotary movements of irregular masses are often extraordinarily erratic, and inequalities are liable to become detached, whereas rotation becomes smooth and even when such irregularities are symmetrically distributed about a centre or central line.

The perfect symmetry of the inert gases (see Chap. I.) is associated with two characteristic properties, volatility and chemical indifference.

Electron shells are not unstable *when they are perfectly balanced* as those of neon and argon prove : it is only when asymmetry is introduced that chemical activity is observed, and tendencies to correct this manifest themselves.

There are three remarkable volatile compounds of the heavy metals, *i.e.* $\text{Ni}(\text{CO})_4$, RuO_4 , and OsO_4 , and it is significant of the connection between symmetry and volatility that not only are each of the four groups surrounding these central atoms similar, but the electron structure of the metal in each instance is very similar; all are perfectly balanced—



the three central atoms merely differ in having one, two, and three quartets in each radial group.

Incidentally this circumstance, like the explanation of the structure of the Rare Earths, affords evidence of the correctness of the electron distribution of the elements which has been advanced.

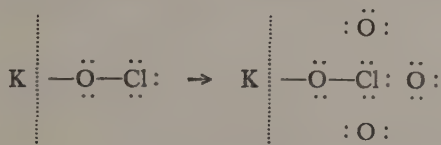
The very remarkable volatile compound basic-beryllium acetate, $\text{Be}_4\text{O} \cdot \text{Ac}_6$, which has been investigated by Sir William Bragg and Prof. G. T. Morgan (P.R.S., 1923, A. 104, 437), has four beryllium atoms and six acetyl groups symmetrically grouped around a central oxygen, the beryllium atoms being tetrahedrally situated (as are the hydrogen atoms in ice), and the acetyls octahedrally.

Twenty-two elements are already known which form compounds of the type MO_4 , most of them belonging to Groups 4 to 7. They are amongst the best defined compounds of these elements, and doubtless owe their stability to the symmetrical disposition of the oxygen atoms around the central one. In the case of the sulphates and molybdates the symmetry is known to be tetrahedral and doubtless this will prove true in many other cases.

Now molecular symmetry can be increased in two ways :—

1. Suitable additions may balance unsymmetrical systems.
 2. Irregular molecules may dissociate into simpler ones.
- Thus, for example, the unstable potassium hypochlorite

gains in symmetry and stability when three further oxygen atoms unite with the chlorine as in the perchlorates, and the symmetry of the system is still further enhanced by dissociation into potassium and perchlorate ions, the external electron structures of which are perfectly balanced—



In fact the celebrated hypothesis of Arrhenius appears to depend on the tendency of unsymmetrical molecules under centrifugal force to divide into portions each of which exhibits increased symmetry.

The investigations of Rutherford and Chadwick on the disintegration of atomic nuclei by α -particles, indicate that the stability of nuclei also depends to some extent on their symmetry, at all events the nuclei containing an *even* number of protons are more stable than those of the odd series.

Atomic Volume.

Some evidence is available that the number of groups or atoms which can be assembled round a central atom is limited on account of their relative sizes or volumes.

For instance, the absence of ions such as CO_4 , NO_4 , and FO_4 corresponding to SiO_4 , PO_4 , and ClO_4 in the next period may conceivably be due to insufficient room for four oxygen atoms in the case of the three former elements. Again, Bragg and Morgan found that when the six acetyl groups of basic beryllium acetate were replaced by propyl radicles, the symmetry of the molecule was appreciably disturbed, the space occupied by the latter apparently could not be accommodated in that which was previously available. In organic chemistry one is frequently confronted with such considerations, and the term "steric hindrance" has been applied to them.

If ample room was available round a carbon atom for

four other carbon radicles, we might expect that the relative positions of the latter would undergo rearrangement under thermal agitation, one group sliding over the atomic surface past another, as it were.

The optical behaviour of many substances sheds a very interesting light on this question. Such rearrangement is actually known to occur under special conditions. For instance either *d*- or *l*-hyoscyamine under the influence of alcoholic potash can be converted into the inactive atropine, which is an association of both the *d*- and *l*-forms, and the latter can always be resolved into these two isomers by treatment with *d*-camphor sulphonic acid and crystallisation, hence *d*-hyoscyamine can be converted into *l*- and *vice versa* at will.

The difficulty in all cases, however, is that we do not at present know how much of such phenomena to attribute to "volume," and how much to the play of electric and magnetic forces operating between the surrounding groups themselves.

The influence of atomic volume has been studied with patience and skill by Dr. Tutton from the crystallographic point of view, from the geometrical standpoint by Pope and Barlow, and from the consideration of density by Kopp, Thorpe, Ostwald, and others. Recently X-ray investigations have provided new data.

Shall we in future have to talk of the atomic volumes of an element in its different states of "oxidation"? *i.e.* does the transfer of an electron from the valence to the potential valence system of an atom affect its volume? An extension of the work already carried out by Lindh and Allison will provide us with more conclusive evidence than is at present available, and enable us to interpret the older indecipherable results.

As regards the elements, a glance at a curve of atomic volumes shows that there is a remarkable difference in volume between the elements of the subgroups in Groups 1 and 2 as determined by density.

Those elements whose outer radial systems consist of quartets only, occupy a much larger volume than those which are surrounded by radial pairs.

The lattice structure of alkali-haloid salts is such as might be expected if the ionic condition persisted in the solid state. We may have to recognise that sodium, etc., in the metallic state consist of $+$ and $-$ ions also, and that ionic structures have their centres further apart than others. This subject is discussed in Chapter VII.

Complex Molecules.

When we consider complex molecules from the standpoint of atomic structure, we find that all the factors which we have traced in atomic association—electrostatic and magnetic forces, symmetry and atomic volume—appear to play some part. A few of the simplest cases are considered below.

Ice.

As probably every one is familiar with Sir W. Bragg's fascinating book "Concerning the Nature of Things" in which an admirable account of the crystal structure and properties of ice is given, it will be unnecessary to discuss this side of the picture here—

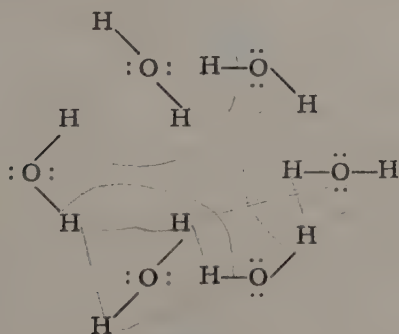


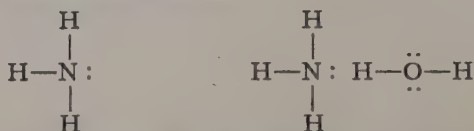
FIG. 2.

From the chemical standpoint the hydrogen nucleus (proton) balanced between the paired shells of successive oxygen atoms is the important feature. Six of these associated molecules form a ring which cannot be satisfactorily expressed by plane formulæ as the four hydrogen nuclei are tetrahedrally arranged around each oxygen atom.

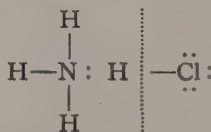
The inner and outer hydrogen nuclei are connected to the paired shells of oxygen atoms of similar rings situated above and below that shown.

Hydrogen nuclei balanced between the valence pairs of other atoms play a very important rôle in adsorption, surface phenomena, and water of crystallisation. Keto-enolic equilibria and certain condensations in organic chemistry are doubtless due to the formation of similar balanced hydrogen structures.

The ammonia type of reaction is a further illustration. Ammonia has a free valence pair, and in contact with water an unstable combination results—



When an acid such as hydrochloric is present, a more stable product is formed, and electrolytic dissociation gives rise to two symmetrical ions—

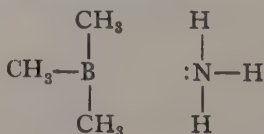


In the ice type of complex a proton lies balanced between two paired electron shells, one of which was originally hetero-valent and the other homovalent.

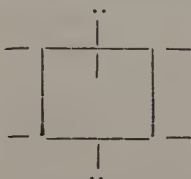
In a second type two atoms are balanced on opposite sides of a homovalent pair.

Examples.

I. Borontrimethide and ammonia combine to form a volatile doubly symmetrical compound. In this case the nitrogen supplies the homovalent pair—

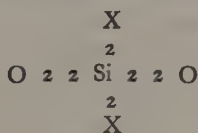


II. Ammonium silicofluoride $(\text{NH}_4)_2\text{SiF}_6$. In this compound X-ray analysis proves that the six fluorine atoms are octahedrally arranged around the central silicon, four of these are, of course, united to the silicon by heterovalent pairs, the remaining two by the homovalent pairs of the fluorine. The attachment of the fluorine atoms relative to the silicon may be expressed in a plane diagram as follows :—



III. Potassium platinichloride $\text{K}_2[\text{PtCl}_6]$. This is similar to the last named and the same diagram serves. In the above examples there are no latent valence or radial pairs around the central atom, in the remainder they are present.

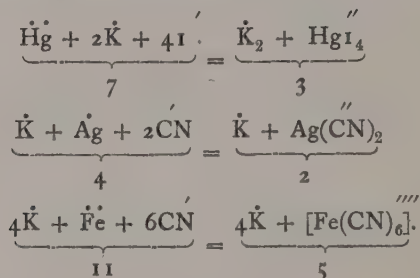
IV. Quartz. X-ray analysis has shown that the crystal unit of this mineral consists of $3(\text{SiO}_2)$. Each silicon has four oxygen atoms arranged roughly tetrahedrally around it. (Bragg and Gibbs, P.R.S., 1925, A. 109, 405). The two oxygen atoms of silicon dioxide are united to the silicon by homovalent pairs belonging to the latter. Two similar molecules unite with a third through the radial pairs of the silicon and the valence pairs of the oxygen at the position marked X—



V. Mercuric and potassium iodides unite to form the complex $\text{K}_2[\text{HgI}_4]$. The two additional iodine ions being united to the central mercury atom like the oxygen atoms in IV.

VI. Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ probably has six cyanogen groups octahedrally arranged about the central iron, four of them being united by the homovalent pairs of the cyanogen, and the remaining two by heterovalent pairs.

In this connection we observe that such insoluble substances as mercuric iodide and silver and ferrous cyanides are readily soluble in solutions of potassium iodide or cyanide respectively, and since crystal analysis has shown that ions preserve their identity to some extent in the solid state as well as in fusions and solutions, it appears that the total number of ions in such systems is diminished—



Therefore the rule concerning solutions “Those ions unite whose product can separate out” is perhaps less fundamental than another which may be formulated as follows: “When ions interact that product is formed which reduces the number in the whole system, solid and liquid, to a minimum.”

Catalysis.

The free paired electrons of molecules are so grouped in crystals that they neutralise each other's magnetic fields. At the surface of such crystals, however, such pairs are ready to react on those of other molecules that may be brought into contact with them. Paired shells of opposite polarity may attract one another magnetically, and adsorption compounds of varying stability are formed. Such interactions may conceivably bring about changes of polarity in certain shells of a molecule, rendering them chemically active towards molecules to which they were previously more indifferent, in other words the surface may act as a catalyst.

CHAPTER III.

THE OXIDATION AND REDUCTION OF TYPICAL INORGANIC SUBSTANCES.

HAVING considered some of the properties of atoms from the standpoint of their external (or valence) electron structure we shall now take their potential valence systems into account.

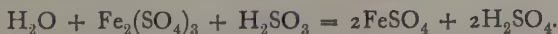
The terms "oxidation" and "reduction" have been applied to several categories of reactions, and it is necessary in the first instance to inquire whether these are strictly comparable.

I. The reduction of ferric chloride by stannous chloride may be regarded as typical of one kind of reduction—



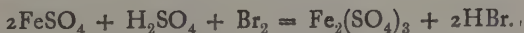
Here the tin is oxidised and the iron is reduced, and the phenomena are associated with an increase in the active valence of one element and a diminution in the other.

Similarly in the reaction—



The iron is reduced and the sulphur is oxidised.

By analogy with the above it has been usual to describe the reaction



as *one in which the bromine is reduced*. This statement will be further considered below; it will be observed that there is *no change in the active valence of the bromine* in this case.

II. When non-metals unite with different proportions of oxygen they are said to undergo oxidation as the active valence of the non-metal increases.

Simple examples are :—

- (1) $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O}.$
- (2) $\text{SO}_2 + \text{I}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}.$
- (3) $2\text{KOH} + \text{Cl}_2 = \text{KCl} + \text{KOCl} + \text{H}_2\text{O}.$
- (4) $3\text{KOCl} = 2\text{KCl} + \text{KOCIO}_2.$

In neither (2) nor (3) is there any change of valence in the halogen. Hence the halogens and hypochlorites can be correctly described as oxidising agents in the sense that they may raise the active valence of other elements, but they are not themselves reduced in the process, *if we define reduction as a process in which the active valence of an element is diminished.*

III. The process of transforming organic substances, such as alcohols, into ketones, aldehydes, acids, or carbon dioxide and water, is described as one of oxidation and *vice versa*. This subject is discussed in Chapter IV.

IV. The operations in which metals are liberated from salts, oxides, sulphides, etc., are generally known as reductions, and the agents employed, carbon, hydrogen, and so on, are known as reducing agents; conversely a metal such as magnesium during combustion is said to undergo oxidation, although there is no reason to suppose its active valence is increased. The fact is that *the term "oxidation" is used in two senses.* In its broader meaning it covers all cases of combustion in oxygen and processes whereby the oxygen content of molecules is increased, and it is also used in a special restricted sense to describe *processes in which the active valence of elements is increased.*

It would, we believe, clarify our ideas and simplify discussion of the subject if the terms "oxidation" and "de-oxidation" were confined to processes in which oxygen is directly concerned. "Bromine water *oxidises* iron from the ferrous to the ferric condition" is somewhat of a misnomer, and the substitution of the word "*activates*" would avoid confusion of ideas.

The word "reduction" is sometimes applied to any process in which the hydrogen content of molecules is increased, for instance, the conversion of bromine into hydrobromic acid, and of ethylene into ethane, have been described

as reductions. It would be better to describe these as hydrogenations, if a special term is necessary, for we shall shortly bring forward evidence to show that an increase of the hydrogen content is sometimes in the nature of an activation (or "oxidation" in the restricted sense).

We shall now proceed to consider the electron phase of the subject.

Eastman's Views.

In 1922 E. D. Eastman (J. Am. C. S., 44, 438) put forward the hypothesis that the two electrons which are recognised as occupying positions within the valence system of atoms, played the part of valence electrons in the case of double and triple bonds. He did not consider the matter as being connected with oxidation and reduction, however, nor did it occur to him that there might be more than two electrons which play a similar rôle, so he was led to conclude that the inner electrons only functioned as valence ones in the case of the elements of the first period.

Eastman adhered to a modified form of G. N. Lewis's eight static electron, cubic valence structure, instead of pairs revolving about centres outside the nucleus, the number and symmetry of which depend on circumstances, as has been employed here. It must stand to the credit of this somewhat inflexible conception, therefore, that it should have lead him to interpret—correctly as we believe—some of the chemical characteristics of the lighter elements, although he thought the restricted freedom of rotation of double bonds was due to two static electrons lying further apart in their case than in that of single bonds.

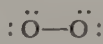
Eastman's views mainly concern organic chemistry, and are referred to in the next chapter, but we must point out here that he suggested that the molecules of nitrogen and oxygen had the electron structure



as expressed in our formulæ, the nitrogen atoms having no inner electrons, and one oxygen having none, and the

other two inner electrons. In both cases the molecules are surrounded by what we have termed latent valence pairs, but which Eastman described in terms of octets.

We think the oxygen molecule may be equally well represented as



each atom having one inner electron, otherwise the structures appear the only probable ones yet suggested.

The Two Kinds of Oxidation or Activation.

If we define the reduced state of an atom as that in which there are the smallest number of active valence electrons or bonds, *i.e.* pairs common to the valence system of two atoms; and the "oxidised" or *activated* state as that in which the number of active valence pairs has increased, then the dissection of electron structures at once reveals the fact that there are two kinds of "oxidising" or activating reactions, which may conveniently be summarised as *basic* and *acidic*, because the products of such reactions have a general tendency to exhibit basic or acidic characteristics, although, of course, these merge into one another in neutral bodies.

Basic Activation.

In this case the latent valence pairs of atoms are separated, *one of the pair is transferred to the potential valence system*, and the other forms a heterovalent pair with the single valence electron of hydrogen or the halogens.

Acidic Activation.

In this case the latent valence pairs of an atom are generally transformed into active homovalent pairs common to the valence system of the atom concerned, and that of another such as oxygen. The oxy-acids of the non-metals are typical examples of such "oxidations."

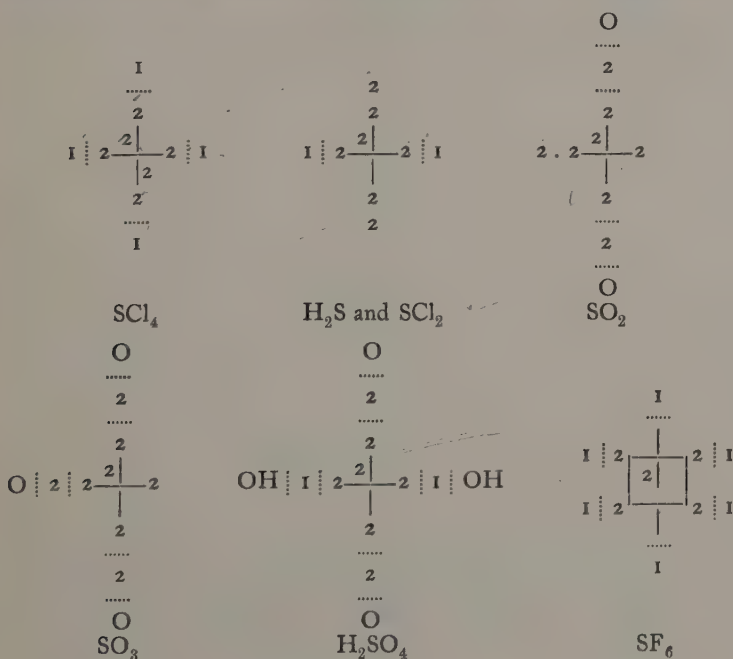
It should be noted that in the higher *basic* "oxidised"

or activated states the number of potential valence electrons reaches the maximum; the minimum number is present in the reduced and acidic oxidised states (*vide* p. 44).

Sulphur A.N. 16.

The electron distribution in the case of sundry sulphur compounds is shown below. It will be noted that sulphur, like phosphorus and the halogens, undergoes acidic activation almost exclusively. The corresponding selenium and tellurium compounds have similar valence distributions.

Sulphur in Sundry Compounds (Se and Te are analogous).



As oxidation proceeds the latent valence pairs are activated in turn.

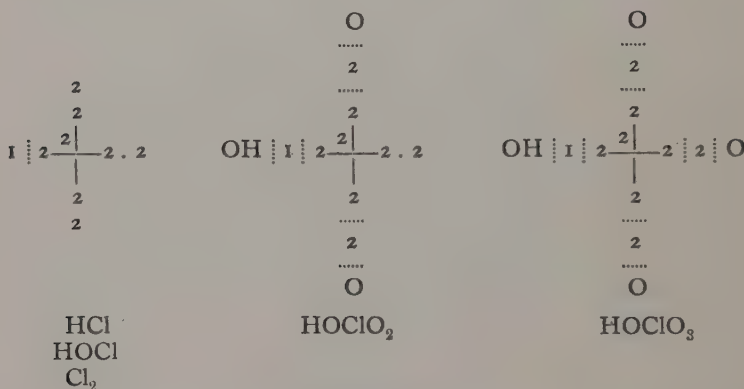
In the diagrams the *active* valence electrons are placed outside dotted lines. Where these are isolated they form heterovalent pairs with those belonging to the valence system

of hydrogen, a halogen or hydroxyl as the case may be : homovalent pairs enter the valence system of oxygen atoms completing their four pairs.

In the case of the persulphates, one of the oxygen atoms probably has only one potential electron and seven valence, as in molecular oxygen and peroxides, unless, as seems less likely, an electron from the potential system of the sulphur passes into the valence system, leaving one potential valence electron only there.

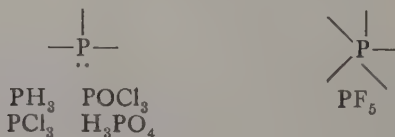
Chlorine in Sundry Compounds.

The electron distribution in the oxy-acids of chlorine are shown below :—



Phosphorus.

The valence electrons only of phosphorus are shown in graphic formulæ, one latent pair is present in PH_3 and PCl_3 , this becomes an active homovalent pair in H_3PO_4 and $POCl_3$ —



Basic Activation or Oxidation.

If the potential valence section of the Periodic Table on page 13 is examined, it will be seen that the two series of salts formed by the members of the palladium and platinum families differ from each other structurally in each case in the same manner. Platinous chloride, for example, has two active valence electrons and two latent valence pairs; when this is "oxidised" to the platinic salt the two latent pairs are split up, two electrons pass into the potential valence system, and two acquire active valence powers.

The elements of the iron family, in their divalent condition, have two active valence and two latent pairs of electrons. On oxidation only one pair is activated, a single electron passing into the potential valence system, the other assuming active valence powers. In every case "*oxidation*" *ceases when there are six electrons in the potential valence system which is evidently the limit of stability.*

As has been pointed out the earlier members of the iron family belong to both sections of the Periodic Table. They undergo both basic and acidic "oxidation" as do nitrogen and carbon, which are for convenience dealt with together in the next chapter.

Chromium and manganese in the chromates and permanganates belong to the potassium period of the valence section their salts being analogous and at times isomorphous with the sulphates and perchlorates. The ferrates complete this series.

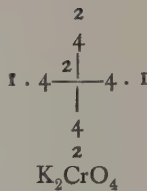
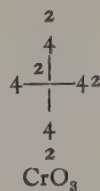
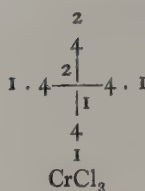
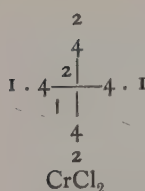
In their basic rôles these elements resemble cobalt as was seen in Chapter I.

The acidic oxidation of chromium and manganese is effected as in the case of sulphur and chlorine, *both* electrons of latent pairs remaining after activation in the valence system in the chromates and manganates. When the manganates are oxidised to permanganates one potential valence electron is transferred to the valence system, *i.e.* in the opposite direction to the movement in basic oxidation.

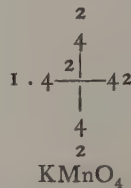
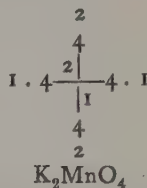
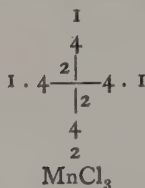
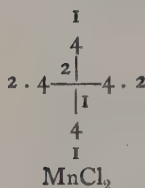
This result is important; the interpretation of the structure of carbon and nitrogen in certain compounds is partly based upon it—

ATOMIC STRUCTURE

Chromium A.N. 24.



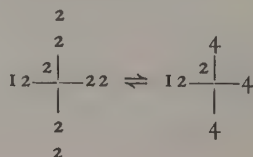
Manganese A.N. 25.



The structure of auric gold is unique and interesting. Ordinarily when metals undergo basic oxidation one or more latent valence pairs are split up, one of the pair joining the potential valence and the other the valence system. Aurous gold, however, already has six potential valence electrons, which is the largest number that the system can accommodate. In this case both the electrons of the latent pair remain in the valence system, and the active valence changes from one to three in one step.

Double Pairs or Quartets?

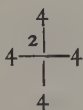
In more complex atoms the pairs inside the valence system obviously tend to form quartets—the radial quartets. It is possible therefore that the double pairs of chlorine, bromine, and iodine and their hydrogen compounds, and those in compounds such as quartz, exist in quartets, and in the formation of the oxy-halogen acids oxidation results in the splitting up of quartets in the first instance, chlorine undergoing a transformation such as



REDUCTION OF INORGANIC SUBSTANCES 41

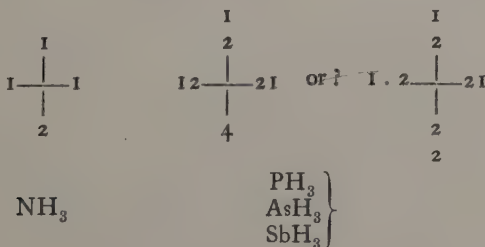
It will be recalled that this actually occurs on the oxidation of cerous salts, where a quartet dissociates, and three of the electrons pass into the potential valence system of ceric cerium.

There is one circumstance which lends support to such a view ; chloride *ions* would then have the same structure as those of potassium, *i.e.*



and it is noteworthy that *these ions have the same mobilities* in aqueous solutions, and hence are used as buffer ions to obviate diffusion potential effects. Moreover there is a considerable difference between the solubilities, etc., of fluorides and chlorides, bromides, and iodides, for instance CaF_2 is insoluble whilst the remaining haloid salts are soluble and deliquescent. Pairs in the former and quartets in the latter would account for their differences.

The feeble basic powers of PH_3 , AsH_3 , and SbH_3 , as compared with NH_3 , may be due to their *two* pairs forming quartets, the *single* latent pair of ammonia having greater attraction for the hydrogen ion—



All these chemical considerations indicate that too much importance is attached to calculations of the work necessary to remove electrons from one level to another. Such calculations are based on theoretical conceptions that may have to be considerably modified ultimately. Nuclear distance is only one factor of stability.

In Chapter II. we showed that the symmetrical disposition of the electrons around atoms varies with the nature of their connections ; in the process of rearrangement it is probable that the forces retaining inner electrons are profoundly modified.

The oxidation of non-metals points to their valence electrons being particularly stable when compared to those of the metals, for they all retain their positions in the valence system. This result may have some bearing on electrical and thermal conductivity. The insulating properties of sulphur, for example, indicate that its electrons are immobile, whilst the conductivity of metals is consistent with free movement.

CHAPTER IV.

THE OXIDATION AND REDUCTION OF ORGANIC SUBSTANCES.

WILL the next fifteen or twenty years witness a minor revolution in the teaching of theoretical organic chemistry, and in its printed and written pictorial representation? Some of the factors that may bring about such a result are ready for consideration—some years may elapse before the verdict can be announced.

Although there are only six extranuclear electrons in the carbon atom, the problem of co-ordinating its chemical behaviour and electron structure is by no means a simple one, and unexpected difficulties connected with chemical phraseology are encountered at the outset.

A comparison of the states of activation ("oxidation") of manganese with those of carbon and nitrogen will perhaps make the position clear.

The electron distribution of manganese, in its basic and acidic "oxidation" compounds, is set forth below in a table—the four radial quartets being omitted for simplicity.

It will be seen that the maximum number of potential valence electrons occurs in the highest basic activation products, and the minimum in the reduction and highest acidic oxidation products; "oxidation" in either direction entails the *activation of latent valence pairs*.

The corresponding tables for typical compounds of nitrogen, carbon, and sulphur are placed below for comparison. The basic oxidation product of nitrogen, ammonia, has two potential valence electrons, the acidic none.

The highest basic "oxidation" products of carbon also have two potential valence electrons, and the higher acidic compounds none. It is here that the absurdity of our

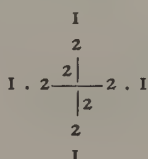
Element.	Compound.	Potential Valence.	Valence.			
			TOTAL.	Latent.	Active.	
Manganese	MnCl ₃ . . .	4	5	2	3	↑ ↓
	MnCl ₂ . . .	3	6	4	2	
	K ₂ MnO ₄ . . .	3	6	0	6	
	KMnO ₄ . . .	2	7	0	7	
Nitrogen	NH ₃ . . .	2	5	2	3	↑ ↓
	N ₂ ; NO . . .	0	7	6	1	
	NO ₂ . . .	0	7	4	3	
	HNO ₃ . . .	0	7	0	7	
Carbon	CH ₄ ; diamond . .	2	4	0	4	↑ ↓
	C ₂ H ₄ ; C ₆ H ₆ ; graphite	1	5	2	3	
	C ₂ H ₂ . . .	0	6	4	2	
	CO . . .	0	6	6	0	
	CO ₂ . . .	0	6	4	2	
	RCOOH. Na ₂ CO ₃	0	6	2	4	
Sulphur	SCl ₄ . . .	4	4	0	4	↑ ↓
	SCl ₂ H ₂ S . . .	2	6	4	2	
	SO ₂ . . .	2	6	2	4	
	H ₂ SO ₄ ; SF ₆ . .	2	6	0	6	

phraseology is most apparent for we are obliged to talk of "oxidising" acetylene to ethane, by the introduction of four hydrogen atoms : a process that has, in fact, been described as one of reduction ! If four chlorine atoms are introduced instead, it sounds, perhaps, slightly less incongruous, yet the process is exactly analogous to the "oxidation" of platinous to platinic chloride. Each platinous atom and each carbon (in acetylene) possesses two latent valence pairs, and on "oxidation" ! in each case these pairs are broken up, two electrons join the potential valence system, and the remaining two are concerned as active valence electrons with the union of the two chlorine atoms. We recognise that the highest

hydrogenated product of carbon has weak basic qualities—when the hydrogen of ammonium hydroxide is replaced by methyl groups, its alkalinity is considerably increased. When ethane is reduced or deactivated to ethylene its basicity decreases—the six carbon atoms of this type in benzene give to phenol its feeble acidic qualities, as compared with the neutrality of water. On further reduction the acid qualities are still more marked—the hydrogen of acetylene is sufficiently acidic to be directly replaced by metals, the degree of acidity or basicity depending, of course, on the nature of the surrounding atoms as well as on the structure of the central one.

The arrows in the table pointing upwards indicate the direction of increasing basic activation, those downwards increasing acidic. Reduction corresponds to diminished activation in either case, *i.e.* an increase in the latent valence.

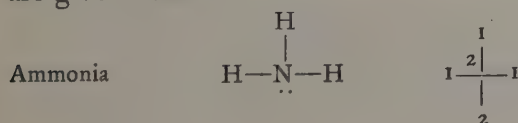
It will now be apparent that both SCL_4 and Pope and Peachey's methyl-ethyl thetine bromide are probably derivatives of the hypothetical SH_4 , $\text{S} =$

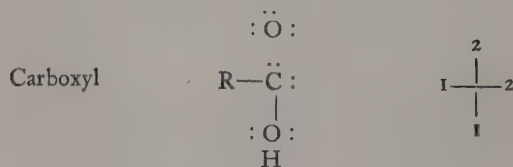
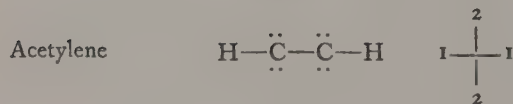
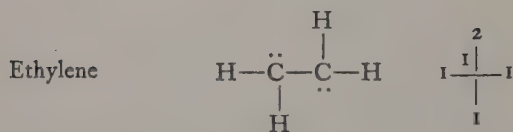
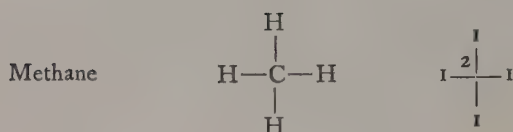
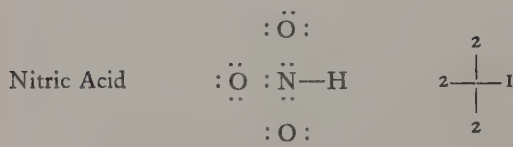
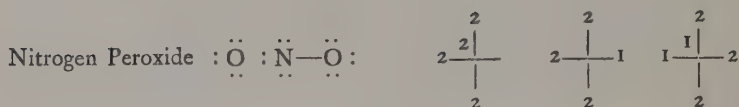
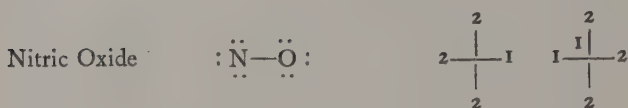
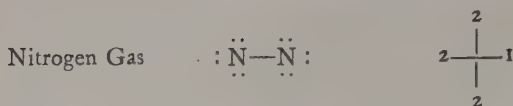


in which the sulphur is present in the state of basic activation.

If the views enunciated here concerning electron distribution are well founded, a new term to describe the process of increasing the active valence of carbon atoms is essential—one which is independent of any element. The term "oxidation" can no longer be used to describe hydrogenation, chlorination, bromination, etc.—"activation" may prove acceptable.

The special graphic formulæ of the compounds in the above table, and the dissected structure of the central atoms, are given below :—





In organic chemistry we have to deal with atoms of the central type connected together, and by the definition adopted in Chapter III. we can only speak about the state of activation (oxidation) of each individual atom. The two carbon atoms of acetic acid are in different states—"the state of oxidation of acetic acid" is a meaningless phrase. It may be repeated here that no complete solution of the problem of activation (oxidation) is being attempted here. From the present standpoint the iron in ferrous chloride and ferrous iodide are identical, as are the corresponding carbon atoms in methane and carbon tetrachloride, or acetic and trichloroacetic acids—the energy phase of the problem and calorific values are not being discussed.

In organic substances there is a marked tendency for nitrogen in the state of acid activation to pass—with loss of energy—into the state of basic activation, or in other words for two of the valence electrons to migrate into the potential valence system. During such changes the oxygen attached to nitrogen is transferred to carbon. Familiar examples are the change of cyanates into isocyanates, ortho nitrophenyl propionic acid into isatin, ortho nitrotoluene into anthranilic acid, the Beckman transformation of oximes, and the decomposition of fulminic acid, and explosives.

Double and Triple Bonds.

In the last chapter attention was drawn to Eastman's hypothesis regarding the nature of double and triple bonds. It is probable that his ideas regarding the valence functions of the inner electrons would have received more favourable attention than they did, had he satisfactorily explained the existence of isomeric substances, such as maleic and fumaric acids. His suggestion that in such cases two *static* electrons lie further apart than in the case of single bonds proved unacceptable.

We have shown above that free paired electron shells (latent valence) are present in the case of a great number of elements, there is therefore nothing inherently improbable in their being associated with carbon atoms.

Indeed the validity of Wislicenus' conception—useful as it has been for the development of organic chemistry—has been called in question more than once in recent times on purely chemical grounds.

Resistance to the free rotation of "unsaturated" carbon atoms may arise from two causes—

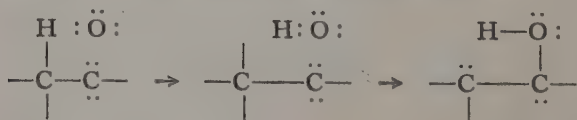
- (1) Hydrogen linkage.
- (2) Magnetic fields.

Hydrogen Linkage.

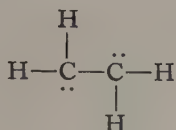
In Chapter II. the structure of ice was referred to, and the manner in which the hydrogen nucleus when balanced between two paired electron shells linked up the oxygen nuclei. The phenomenon is probably a very common one, and plays a more important rôle in chemistry and physics than has been suspected. Whenever the kinetic movements of molecules containing hydrogen bring them into the neighbourhood of the suitably phased latent valence pairs of other atoms whether of solids or liquids, some association more or less stable probably occurs, and a state of equilibrium is established.

In the case of organic compounds hydrogen linkage occurs between the different atoms of the same molecule as well as between those of different molecules.

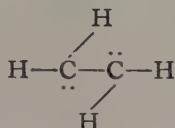
The most fully investigated case is that known as keto-enolic tautomeric change, in which a hydrogen nucleus is attached to both a carbon nucleus and that of a neighbouring oxygen, lying at times balanced between them—



We must expect therefore that hydrogen nuclei will connect the latent pairs of contiguous carbon atoms, when these are present, and although it is convenient to formulate ethylene as



it may be more correct to depict it as



The Magnetic Fields of Carbon Atoms.

The directional effects of the magnetic fields in atoms has been considered in Chapter II.

There is no obvious reason why electrons should rotate in their orbits in one direction rather than another, but their magnetic fields as seen from the adjacent nuclei of carbon chains must be of opposite sign, for if an electron shell presents its north pole to one, its south is turned towards the next, hence adjacent carbon atoms are not magnetically identical.

The nature of the chemical difference between the alternate carbon atoms in both straight chain and ring compounds, has given rise to much discussion during recent years. A short summary of the literature on the subject is given by Professor C. K. Ingold in the preface to one of his earlier papers on "The Nature of the Alternating Effect in Carbon Chains" (J.S.C., 1925, 127, p. 513).

These directive forces are the intra-molecular counterpart of those which determine the alignment in the case of crystals, and compel each molecule, as it is deposited on a crystalline surface, to assume its appropriate orientation. The magnetic fields around carbon atoms probably play an important directional part in the case of latent valence (free bonds).

The presence of latent valence pairs explains the "shifting of double bonds" that has been observed in certain compounds. For instance, during the limited bromination of Thiele's conjugated double bond compound

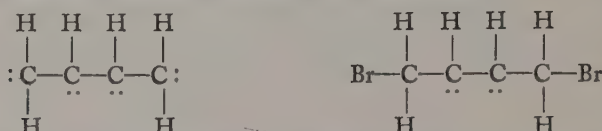


a dibromide is formed which is usually represented as



the reaction being accompanied by a shift of bonds.

If, however, the hydrocarbon is expressed in terms of latent valence it is seen that no shift occurs—



the terminal atoms merely undergo basic activation. In other cases tautomeric changes occur which point to hydrogen bridging valence pairs.

Thus the change of propyl acetylene into methyl-ethyl acetylene



can be pictured as resulting from the fission of an unstable four membered ring

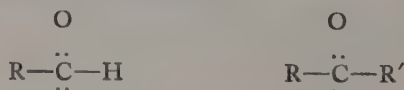


a repetition of the process resulting in the formation of the above isomer.

The Latent Valence of Aldehydes and Ketones.

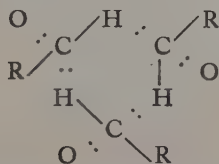
The characteristic "properties" of these substances include the formation of condensation products on the one hand, and addition compounds with such reagents as acid sulphites, hydrocyanic acid, ammonia or Grignard's reagent on the other.

It has been usual to ascribe this behaviour as due in some unexplained way to the presence of oxygen attached by a double bond to carbon. A more probable explanation is that the centre of attraction is a free latent valence pair or free bond attached to the carbon—



Here all six extranuclear electrons of the key carbon atom are in the valence position.

On this view the condensation of an aldehyde is due to a similar cause to that which brings about the formation of ice from water. In the latter case the hydrogen nuclei link up the oxygen atoms through the free latent valence pairs of the oxygen, in the former they connect up the molecules through the latent pairs of the carbon and a heterocyclic carbon-hydrogen ring is formed—

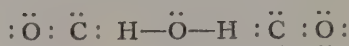


The old valence doctrine misled chemists. It is probable that no factor in organic chemistry has been underestimated so much in the past, as the ability of hydrogen to connect up with latent valence in this ice-like manner. It probably decides the course of many combinations, condensations, and hydrolyses. The combination of chloral with water and alcohol to form chloral hydrate and acetal, the aldol type of condensation, and Perkin's reaction, are a few instances. In Cannizzaro's transformation of aromatic aldehydes into alcohols and acids, the addition of water must precede disruption.

During combustion processes intermediate substances are probably formed, in which two molecules connect up, in the first instance through the hydrogen nucleus becoming balanced between two electron pairs—one of which was previously a latent pair.

The wonderfully interesting results of Professor H. B. Baker's skilful work on the difficulty of inducing combination in dry gaseous mixtures, that usually give rise to explosive reactions, and the modified physical properties of well-dried liquids, indicate that we have yet to understand the importance of the part played by the balanced hydrogen nuclei of associated water molecules. There are three latent pairs about each carbon atom in carbon monoxide, and the fact

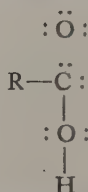
that Professor H. B. Dixon in 1880 discovered that its admixture with oxygen, when dry, failed to explode on sparking, indicates that ordinary carbon monoxide may contain a small proportion of associated molecules, where the hydrogen is balanced between the pairs of oxygen and carbon atoms, water possibly connecting two molecules thus—



and that a high local temperature induces reaction between this “intermediate” and oxygen. A dozen such schemes could, however, be drawn up.*

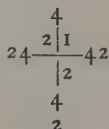
Fatty Acids.

The presence of the latent valence or free bond in fatty acids is not so evident as in the case of the aldehydes—



Its presence may account for the fact that the lower fatty acids exhibit molecular association—the vapour density of acetic acid near its boiling-point is abnormal.

Perhaps the most direct evidence we have concerning the free carbon bond in carbonates and carboxylic acids, is that afforded by the existence of two series of cupric salts. Cupric copper is exceptional in having an unsymmetrical radial system beneath the valence system—omitting the latter this appears to be



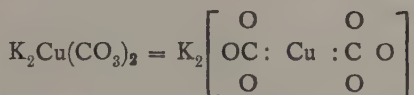
* An excellent account of certain combustion processes is to be found in Bone and Townend's recent work “Flame and Combustion in Gases.”

and this is probably the reason why copper in certain organic substances exhibits unique features.

In addition to the ordinary ionisable salts, copper forms carbonates, citrates, tartrates, etc.—the solutions of which possess a deep blue colour—from 10 to 20 times the intensity of copper sulphate solutions of equivalent strength. Many of these have been isolated—some only as double salts—and the investigations of S. U. Pickering proved that in them *the copper was directly united to the carbon*.

In these salts the copper forms part of a negative ion, and on electrolysis migrates to the anode ; it is not deposited on metallic iron, nor precipitated by alkaline solutions generally. When warmed with glucose, cuprous oxide is formed as in Fehling's reaction.

In the simplest cases the copper probably directly connects two carbon atoms, for instance



The behaviour of fatty acids and their salts in films and soap bubbles may be partly due to the free bond of the carboxyl. The long chains of fatty acids stand end-on "like corn in a field" as Sir Wm. Bragg has put it, at right angles to the surface of the films, the carboxyls being immersed in the water and the methyl groups in the air. The preference of the carboxyls for water may be due to hydrogen linkage with the free carbon bonds.

The attractive forces which appear to exist between parallel aliphatic chains are perhaps of magnetic origin. If the magnetic character of carbon atoms alternates in chains, the terminal methyls of natural fats, which all belong to the even series, are presumably alike, and of opposite sign to that of the carboxyl. These similar magnetic fields may be the cause of the curious mutual repulsion between well-drained bubbles observed in Professor Boys' well-known experiments.

Valuable information might be obtained by preparing acids of the odd series by Le Seur's method, and studying their

behaviour towards the former in the presence and absence of external magnetic fields.

Quinones.

The chromophoric characters of these substances are discussed in the next chapter, but it may be pointed out here that all difficulties regarding the distribution of double bonds are swept away when these are abandoned, and the naphthaquinones and benzoquinone fall into line. Apart from the fact that the carbon atoms associated with the oxygen have all six electrons in the valence positions, the aromatic nucleus remains unchanged.

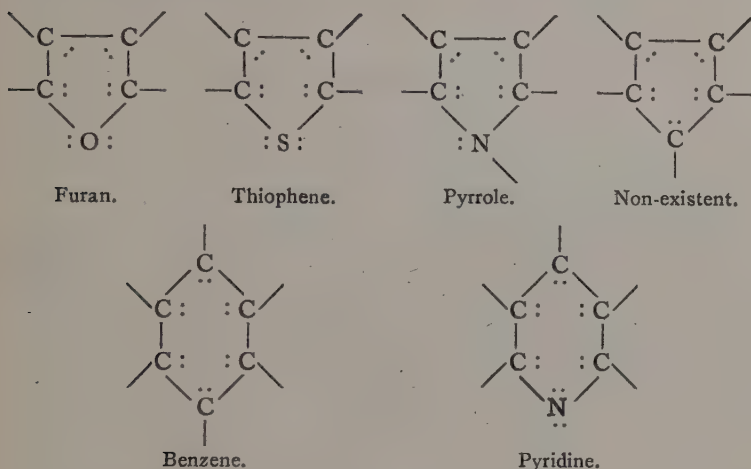
Cyclic Compounds.

The reactivity of latent valence pairs varies enormously. Their presence in neon and the fluorides is not suspected from chemical considerations. The six pairs round each molecule of oxygen or nitrogen, and the eight around that of carbon dioxide are hardly obtrusive. Their influence in building up the complicated silicates has yet to be realised, though the patient and admirable researches of Sir Wm. and Professor W. L. Bragg is beginning to attract attention to their chemistry once again. At present inorganic chemistry is the science of unrecognised latent valence—and ions.

In organic chemistry, on the other hand, great attention has been paid to the supposed double and triple bonds of "unsaturated" carbon, nitrogen, and oxygen, and a large speculative literature devoted to the structure and bond distribution of benzene alone exists. As the importance of the potential valence system is realised, a more general view of latent valence will become possible, and the present hard and fast tests for unsaturation will be abandoned, or at least modified conclusions will be possible; undue regard for these tests has led us to ignore the presence of "free bonds" in many cases.

If we consider the five membered "unsaturated" cyclic nuclei we are struck at once by the fact that there is no pentacyclic carbon nucleus with benzene-like properties

corresponding to furan, thiophene, and pyrrole. This fact raises an important question—Are the latent valence pairs of unsaturated cyclic carbon atoms associated in pairs of opposite magnetic polarity?—



Each carbon atom here has five valence electrons and one potential valence.

In terms of bonds benzene above appears identical with that put forward by Professor H. E. Armstrong (J.C.S., 1887, 51, 264), but it is important to remember that adjacent and opposite carbon atoms are not magnetically identical here.

At first sight this would seem to imply the existence of two monosubstitution derivatives, but magnetic polarity is probably a labile property, capable of reversal under the conditions which prevail during replacement.

In heterocyclic rings the non-carbon atom as in pyridine, quinoline, and isoquinoline may behave magnetically like a carbon atom or (as in the pentad rings) the free bonds may have an independent existence.

Para Changes.

The association of the latent valence in opposite pairs goes far to explain the tendency for certain aromatic transformations to result in para substitution. The conversion of

aniline sulphate into sulphanilic acid is a typical case. Under thermal agitation the magnetic ties of the unbalanced compound are loosened and rotation of the para carbon atoms facilitates rearrangement. This para association has often been suspected but was difficult to explain on older lines.

Condensed Cyclic Compounds.

All the carbon atoms of benzene are in the same state of activation, and have but one potential valence electron. In condensed rings the atoms common to two rings are probably more completely reduced, and have all six electrons in the valence system—four of them forming two latent pairs. Naphthalene in terms of bonds (and omitting magnetic considerations) on this view appears as in Armstrong's formulation—



Fortunately X-ray analysis is likely to come to the assistance of organic chemists, by resolving many of these obscure problems. Already facts are accumulating—such as the investigations of Lindh and Allison have brought to light—relating to the variation of level of an electron in certain atoms, with the “state of oxidation” of the compound examined.

As physicists learn to interpret records in terms of potential valence, they will doubtless discover the true electron distribution of carbon in its simpler combinations, and the existence of latent pairs will be confirmed or disproved.

CHAPTER V.

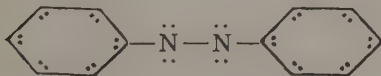
THE NATURE OF THE CHROMOPHORES.

No phenomena intimately connected with activation and deactivation (oxidation and reduction) present problems of greater scientific and industrial importance than those which are concerned with colour.

The energy required to bring about changes of state varies greatly, and in many colouring matters the movement of an electron under the influence of incident radiation appears to create a state of dynamic equilibrium: at one moment it is transferred from the potential valence system of one atom A, to that of an adjacent atom B, A and B being "charged" positively and negatively respectively, in the next it returns to its original position, the process being repeated indefinitely.

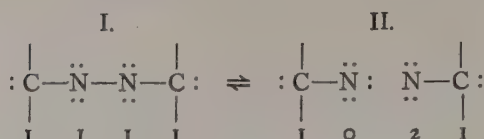
The physical significance of these migrations is discussed in Chapter VI., meanwhile we shall consider some typical examples of chromophores.

Azo Dyes.



The two nitrogen atoms of azo compounds are usually regarded as being the chromophoric grouping, although it is possible that the carbon atoms attached to them are also active.

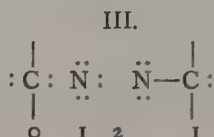
If we dissect out these four atoms we note that their electron distribution may be arranged in several ways. In I. each carbon and nitrogen has one potential valence electron,



In II. one nitrogen has two potential valence electrons and the other none.

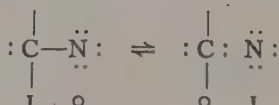
The figures placed beneath the key atoms in these examples and those which follow, indicate the number of electrons in their potential valence systems.

If migration between the carbon and nitrogen also occurs, the state shown in II. might change to that in III.



Nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$.

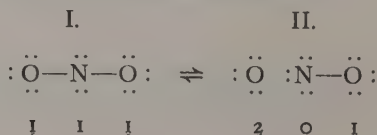
The chromophore here is probably the carbon-nitrogen bond; dissecting this out there are two possible structures which may co-exist in dynamic equilibrium:—



In the first the potential valence systems of the carbon and nitrogen contain respectively one electron and none, in the second none and one.

Nitrogen Peroxide.

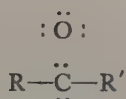
The chromophore of the dark simple molecule may be that suggested in the following scheme:—



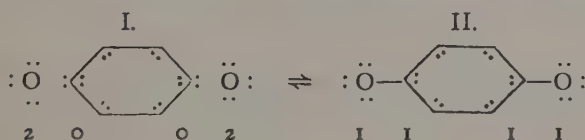
In I. there is one electron in the potential valence system of each atom ; by migration from the nitrogen one can be transferred to either of the oxygen atoms.

Quinones.

The structure of ketones, which has been put forward in Chapter IV., appears to hold good in the case of quinones of all types—



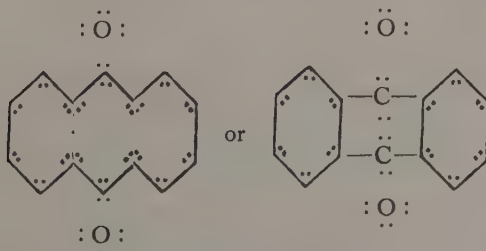
these, however, probably exist in tautomeric forms, which in the case of benzoquinone may be formulated as follows :—



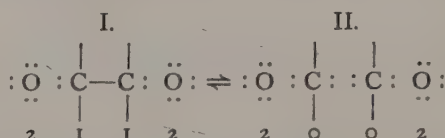
In I. the oxygen atoms have two potential valence electrons, and the carbon atoms to which they are attached none. In II. the carbon and oxygen atoms each have one potential valence electron. The colour being due to the ready transformation of I. into II.

Alizarin.

It is not known if this contains three or two aromatic nuclei, *i.e.* whether it is best represented by I. or II.



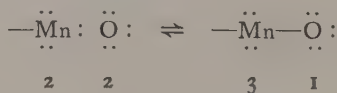
In the latter case the chromophore may not be merely that of a quinone only—the central carbon atoms to which the oxygens are attached may be weakly united as in the case of acridine, which is considered below, and it may exist in two forms like the latter—



In I. the carbon atoms are connected and form a chain, whilst in II. they are separated. In both cases the interchange of an electron between the potential system of the oxygen and the carbon, as in the case of quinone, can occur.

Permanganates.

In the oxidation of *manganates to permanganates* one potential valence electron of the manganese passes into the valence system, Chapter III. Probably the play of forces is such that an alternative peroxide form is possible, in which an electron of the potential valence system of *the oxygen* has passed into that of the manganese—



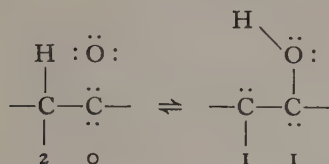
the migration of the electron between the potential systems of manganese and oxygen giving rise to the strong characteristic absorption of permanganates. A similar explanation can be given in the case of the manganates, chromates, and bichromates.

Keto-enolic Substances contain a chromophoric grouping that causes absorption in the ultraviolet region of the spectrum. They have been the subject of spectroscopic investigations conducted by Hartley, Baly and Stewart, and other workers.

These substances contain groupings, which in their extreme forms may be represented as follows :—

I.

II.



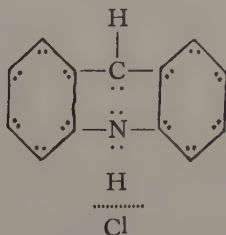
The labile hydrogen is attached to carbon in the first case and oxygen in the second, and the chemical properties of the substances vary according to the type or proportion of the types present, and the rate at which one is converted into the other.

If an electron migrated from the potential valence system of one carbon atom into that of the next carbon atom, the negative charge on that side, acting on the positive hydrogen nucleus, would direct the latter towards the oxygen, the formation of the hydroxyl group being the result.

In the four examples which follow, more decided indications of *incipient dissociation* are apparent: in each case two portions of a complex molecule appear to undergo some separation, followed by recombination of *the same portions*.* The migrating electrons in such cases, perhaps, merely pass from the potential valence system to the valence system, and return back again.

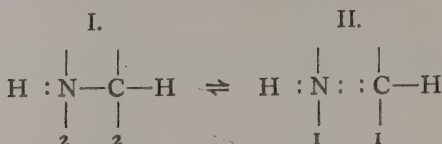
Acridine Dyes.

In the case of acridine salts it seems probable that the central carbon and nitrogen atoms are only feebly united, and the connection between them is readily severed—



* This circumstance distinguishes intramolecular dissociation from electrolytic and thermal dissociation, where combination occurs between *different* successive partners in general.

Dissecting out these two atoms we can suppose that their electron structure varies between the extreme forms I. and II.



In I. each nitrogen and carbon atom has two potential valence electrons, and in II.—where they are no longer united—they have one each.

When the two paired latent valence shells of the separated atoms recombine they may temporarily form a quartet which subsequently undergoes further change into I.

The Rosaniline Chromophore.

The nature of the chromophore of this group in terms of bonds has never been satisfactorily cleared up. The "quinoid" explanation that has held the field for some years is merely the least unsatisfactory—there are several difficulties in connection with its acceptance that were never met.

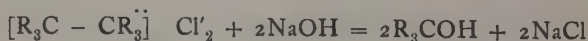
Von Baeyer pointed out that the salts of tri anisyl carbinol—for which a quinoid structure is impossible—behave like those of a member of the group



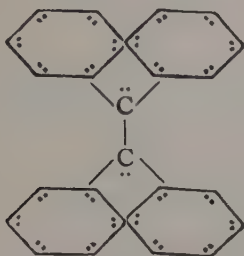
the hydroxyl here as in all members of the class being of the basic type, as in ammonium hydroxide. The simplest explanation of its behaviour is that a condensation of the triphenyl methyl type has taken place—



Further, when the salts of crystal violet are neutralised by just sufficient alkali, a very considerable interval elapses before the base is set free. If the salt were of the ammonium type it would be liberated at once, whereas the reaction



requires time for the dissociation of the complex molecule. Again, di-diphenylene ethylene has a strong red colour which cannot be quinoid—



These facts all point to the rosaniline bases forming complex cations when neutralised by acids. It must be noted, however, that there is a fundamental difference between the condensed form of triphenyl methyl and triphenyl carbinol; the former condenses to hexaphenyl ethane

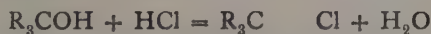


or dissecting out the central carbon atoms



Before condensation each carbon atom has one latent valence pair and one potential valence electron, afterwards each carbon atom has two potential valence electrons. This latter compound is colourless. The colour is connected with electron migration during condensation, and dissociation from one type into the other.

Triphenyl carbinol R_3COH , on the other hand, is colourless, and the salts

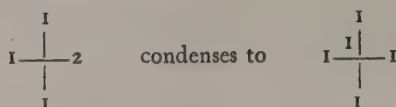


become coloured only as the cation undergoes condensation.

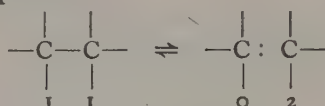


The difference in structure between this complex cation and the hexaphenyl ethane above is this, each central carbon atom here has transferred an electron to the chlorine and has only *five extranuclear electrons—not six*.

Dissecting out the carbon



This complex cation is even more unstable than the former because the electrostatic force of the positive charge in each half tends to force the two portions asunder, and as the potential valence system of each of these carbon atoms only contains one electron each, the process of alternate activation and deactivation proceeds—

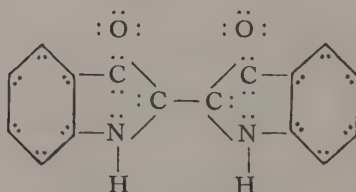


the potential valence systems containing one or two electrons or none in turn.

In both triphenyl methyl and rosaniline the chromophoric carbon has but one potential valence electron left, in the former this phase occurs in the simple molecule, whilst in the latter, owing to ionisation, it is in the complex molecule.

Indigo.

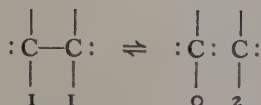
The weak bond between the two central carbon atoms, which is very readily severed, appears to be the chromophore here—



It is possible that an equilibrium exists between double and single molecules as in the case of triphenyl methyl, the key carbon atom having alternately the structure



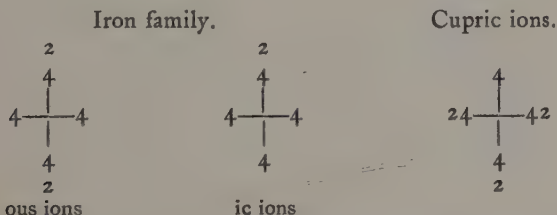
Even if the molecule does not actually dissociate, the migration of an electron from the potential valence system of one carbon atom to that of the other and *vice versa*, may proceed as follows :—



Coloured Cations.

In the case of certain cations the instability appears to be connected with the dissymmetry of the outer electron structure of the cation itself.

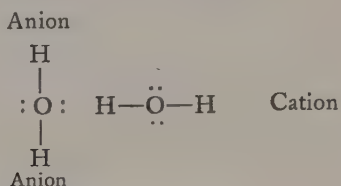
Reference to the valence section of the Periodic Table on page 11 will show that the aqueous solutions of the nitrates, chlorides, etc., of those metals whose cations are symmetrical, are generally colourless, whilst the solutions of unsymmetrical cations, such as those of the iron, palladium, and platinum families, cupric copper, and auric gold, are more or less coloured. These elements have *unsymmetrical latent valence pairs around their ions*,



and are very prone to combine with other molecules to form double salts and complex ions. In some cases at least there is reason to doubt if their colour is an inherent property of their structure as such, rather than to association with the solvent. Some of the cupric, cobaltic, chromic, and ferric salts, which are strongly coloured when hydrated, *are almost colourless when anhydrous*.

Molecules of water of crystallisation in salts appear to function in two ways : I. Some are connected to anions and II. some to cations.

During the process of crystallisation the first perhaps connect the different layers of the anions together, and the second the cations of the intermediate layer either to each other, or to the oxygen of the first class,



just as in ice some of the hydrogen atoms are members of the rings, and others connect these rings together.

All the above cations have unsymmetrical latent valence pairs, and their colour may be enhanced or due to their association with the water molecules increasing the atomic dissymmetry.

The Rare Earths.

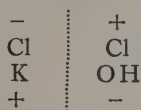
The colour of the ions of the rare earths are not without interest. Those in which the four radial groupings are similar are colourless. When two of the radial groupings are of one kind and two of another the ions are more faintly coloured than when three are of one kind and one is different (Chapter I., p. 15). Cerium is in every respect unique: the ceric salts are strongly coloured, and pass by the extraordinary change on reduction into cerous salts with a modified external radial system. It would appear that the position of the three electrons, which leave the potential valence system in cerous salts, are already so insecure in ceric salts that they give rise to dissociable combinations within the valence system.

The Halogens.

The molecules of iodine vapour dissociate into single atoms at high temperatures, as do those of bromine at still higher temperatures, the colour intensity of the halogens is therefore in the order of their dissociability, and at ordinary temperatures incipient dissociation probably occurs.

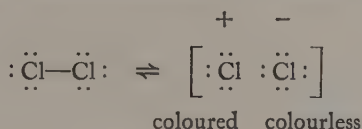
The ions of the halogen salts are of course colourless.

Professor Noyes has pointed out that the chemical behaviour of chlorine towards alkali is that of mixed + and - atoms



equal molecules of chloride and hypochlorite being formed by association with the ions of the alkali hydroxide.

Perhaps the halogens therefore tend to dissociate into positive and negative ions, the heterovalent pair connecting the united atoms remaining attached to one of the partners—



The colour of the unsymmetrical three-shelled positive ion would be due to the same causes as that of the coloured cations considered above. The mechanism of this is considered in Chapter VI.

Such ions need not be regarded as forming separate molecules, like those which take part in conduction; they may form electrostatically united, charged semi-molecules, like the undissociated portion of salts.

CHAPTER VI.

THE EMISSION AND ABSORPTION OF RADIATION.

THAT the movements of the potential valence electrons are intimately connected with the photo-activities of chromophores can hardly be doubted, all the chemical evidence examined in Chapter V. points in their direction ; but if we are to realise what is happening in chromophores it is necessary to form some picture, however imperfect, of the oscillatory processes that cause or affect radiation.

An Oscillating Electron Theory.

When electrons revolve uniformly in spiral fashion about circular orbits, their motion gives rise to magnetic fields—radiation is neither absorbed nor emitted. It is only when the electrons are sufficiently displaced from their orbits that the forces of recovery cause them to oscillate about their orbits periodically, before settling down to smooth spiral motion again. Such periodic motion may be associated with absorption and emission.

Now the shells of spiralling electrons which are distributed around nuclei may be subject to *two* displacements, each of which may *entail periodic oscillations on recovery*.

- (1) Displacements in the direction of the nucleus.
- (2) Displacements of the electrons in the plane of the orbit, *i.e.* at right angles to the former.

Now the elasticities of the shells in these two directions, or the forces tending to push the electrons back into their original orbits when they have been displaced, may be very different. That in the direction of the nucleus may be many times that at right angles to it.

The periodicity of the first would depend chiefly on the

nuclear charge and distance, although the proximity of other shells would exert some influence.

Disturbances of the first type might well follow bombardment from without, and give rise to high frequency oscillations and X-rays, the displacement in the direction of the wave front being connected with the Compton effect.

The second type of displacement is probably concerned with colour and low frequency oscillations.

The two disturbing factors that cause electrons to oscillate periodically are :—

High temperature ionisation—this is responsible for line spectra.

Low temperature shell movements—this determines the properties of many chromophores.

High Temperature Ionisation—Collapsible Shells.

The electrons of the valence and radial systems of atoms in their stable compounds form magnetic shells containing two or four electrons. The stability of these two systems is presumably connected with the symmetrical disposition of the electrons in approximately elliptical or circular orbits.

During high temperature ionisation, however, unstable associations of brief duration, in orbits containing 1, 3, 5, 6, etc., electrons may be formed, and such systems may play an important rôle in line spectra.

The introduction of electrons into an orbit would at once lead to an increase of the orbit through electrostatic repulsion, and on the collapse of the inflated shell the remaining electrons would execute periodic spiral oscillations before settling down to smooth motion in the smaller orbit. The fine structure of the periodic motion would be affected by the ellipticity of the orbit, neighbouring magnetic shells or fields (Zeeman effect) and electric fields (Stark effect).

Let us picture an ionised valence shell containing m electrons. Owing to its unstable character the system collapses, and a new system is formed in which the shell contains a smaller number of electrons n .

This number n is not necessarily always the same, it would depend on the circumstances attending the collapse.

The changes in such a system would correspond to those set forth mathematically in Balmer's general equation connecting the wave lengths of related spectral series.

$$\lambda = C \frac{m^2}{m^2 - n^2}$$

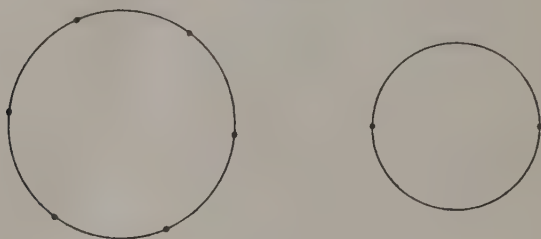


FIG. 3.

Diagrammatic representation of an ionised shell ($m = 6$) and the same after collapse ($n = 2$).

If n had the value 1, 2, or 3 the series would belong to the Lyman, Balmer, or Paschen series respectively.

The orbits m and n are not coplanar, for the elasticities and nuclear distances vary with the diameter and number of electrons in an orbit, hence the electrons in travelling from the first to the second orbit oscillate temporarily about the smaller orbit with a frequency which depends partly on the acceleration acquired during the migratory stage.

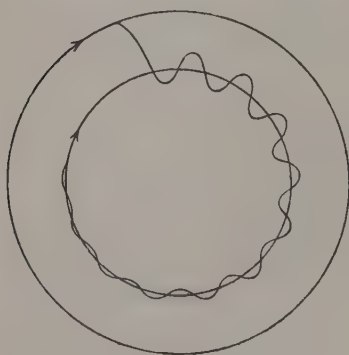


FIG. 4.

The periodic motion of one of the electrons consequent on the collapse of an ionised shell is shown in a purely diagrammatic manner

in Fig. 4. No attempt being made to show the fine spiral movement on the trace of the electron.

The effective amplitude of the periodic motion is perhaps confined to some few hundred vibrations.

Line Absorption.

In this picture the same oscillating shell emits and absorbs—the phenomena are merely a question of the relative intensities of the “source” and the “absorbing medium.”

A beam of monochromatic light may consist of innumerable independent disturbances of the same frequency, each very rapidly quenched.

Such ethereal music would resemble the jumble of sounds set up by members of a large orchestra tuning up independently to the same note, rather than the sustained note from a continually vibrating tuning-fork. But the character of such vibrations would appear to fit in with the known facts concerning interference. Interference is only observed in the case of light from the same source—portions of the train of waves from one collapsible shell must be utilised—two sodium flames will not answer, no two electron shells are quite in unison.

The mechanism of emission envisaged here has some features in common with the celebrated system of Professor Nils Bohr. The atoms according to the latter contain a number of arbitrary *planetary* orbits in which a single electron revolves, passage from one of which to another is associated with emission. Professor Bohr's system, however, admits of no oscillatory movements of electrons, and the mechanism of absorption is entirely different in the two cases. Moreover, the electrons in the present system do not move in planetary fashion, but rotate about symmetrically placed centres, which are situated outside the nucleus.

Band Absorption and Emission. The Movable Shells of Chromophores.

When the paired shell of an atom shifts its position round the rest of the structure, or pivots about the nucleus, the smooth rotation of the electrons in their orbits is upset,* and a periodic motion about the orbit is temporarily set up, of the type depicted in connection with line spectra; but owing to the constraining effect of association with other

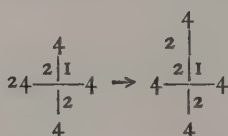
* *Vide* Appendix.

atoms, the periodic movements are somewhat more complex, every motion of one shell being reflected to some extent by those around it.

There appear to be at least two distinct factors concerned in causing the paired shells around atoms to shift their positions, under the influence of incident radiation.

I. The unsymmetrical distribution of paired shells around coloured cations, which was considered on p. 65.

The latent pair of the ferric *ion* may be taken as a type. In plane diagrams a change in its position may be represented as below—



The disturbance of the electrons in their orbit may be attributed to the movement of the paired electrons, and the lack of uniformity of the magnetic field around the nucleus.

II. ELECTRON MIGRATION.

Simple Ejection.

When physicists study the photoelectric behaviour of a substance they determine the conditions under which electrons *leave* the substance when radiation of some kind acts upon it.

Ejection and Capture.

In dye chromophores radiation brings about ejection, but owing to the conditions of association the ejected electron is captured by the next atom, and it (or another) is subsequently returned to the original atom.

The extrusion of this potential valence electron causes some temporary reorientation of the four valence pairs surrounding the nucleus of such atoms as carbon, nitrogen, oxygen, etc.

Body Colour and Surface Colour.

As an example of the mutual relationships between incident radiation and the periodic movements of the electrons in a readily disturbed shell, let us consider potassium permanganate (p. 60), which was carefully studied by Professor Sir G. G. Stokes.

In dilute solutions the vibrating shells absorb certain rays in the yellow-green, and six absorption bands are found there. The remainder of the light is transmitted, and is the cause of the characteristic purple body colour of the substance.

It was pointed out above that all shells emitting line spectra probably act as absorbing shells as well. In chromophores the truth of the reverse is seen. All absorbing shells also emit. The surfaces of crystals of permanganate emit a greenish light—their surface colour—which Sir G. G. Stokes proved to consist of the rays that are absorbed by the solution. Haidinger has shown that the crystals of many dyes also, emit those surface colours which their solutions absorb. Surface colours are not therefore merely reflected light. The incident radiation stimulates the permanganate to emit the yellow-green rays, but the simultaneous absorption prevents such rays from being transmitted or emitted except at the immediate surface. This surface emission is probably of more universal occurrence than has been realised. Generally it is too feeble to be readily recognised as such, and we ignore its existence in such phrases as “the reflected coloured rays are mixed with reflected white light.” The fluorescence which most substances exhibit when exposed to ultra-violet rays in a dark room is, perhaps, but a phase of this phenomenon.

These surface colours are not polarised, and when the crystals are examined through a Nicol prism by light incident at the polarising angle, the reflected body colour can be extinguished, and the surface colour is then alone visible.

This fact is discussed in connection with polarisation at the end of Chapter VIII.

Anomalous Dispersion.

The interaction between the incident radiation and the movable shells is not sharply confined to waves of a particular frequency. Those of appreciably higher frequency are constrained with some loss of frequency, and perhaps those of lower frequency with gain of frequency, hence the spectrum of the transmitted light frequently has the order of the colours near the absorption band inverted.

The phenomena recall acoustic analogies. Resonance columns, for instance, can be caused to vibrate by tuning-forks whose periodicity is very appreciably different from that of the resulting note, and beats may be heard between the two.

The Incident Radiation.

Colour is due to the periodic movements of electrons. It seems probable that these movements are induced by the radiation itself. Where the production of colour is associated with the migration of an electron as in dyes, the internal ionisation may be brought about by higher frequency radiation that has little relation to the radiation that is concerned in the band absorption of the same body.

This preliminary ionising action of somewhat higher frequency radiation is doubtless responsible for the phenomena of *Fluorescence* and it may complicate the phenomena of anomalous dispersion. When the radiation is withdrawn the periodic vibrations cease, although in many cases the cessation is not instantaneous, for the Becquerels have proved by means of the phosphoroscope that the surface colour emission continues for the fraction of a second (*Phosphorescence*).

In the absence of external radiation such substances as chlorophyll, dyes, and permanganates may be as colourless as common salt in the periodic vibration sense.

The speed at which these reactions proceed is amazing ; it tends to obscure the comprehension of the mechanism of chromophores in slow motion.

Periodic vibrations are set up and absorption commences

in a minute fraction of a second. But we should not perhaps have suspected radiation of being capable of bringing about the complex phenomena associated with the taking of a photograph in the $\frac{1}{500}$ of a second, unless methods of developing the latent image had been devised.

Although the phosphorent phenomena of chromophores are usually associated with periods of a few thousandths of a second, and possibly even less, in other cases the action of light leads to migrations and more complex changes which require a considerably longer interval for the establishment of the equilibrium.

The changes in the conductivity of selenium on exposure to light (Chapter VII.) require quite a minute for completion.

The decomposition of the vapour of pure anhydrous nitric acid by sunlight—which does not act on the liquid form—in sealed tubes, in vacuo, reaches a maximum in a few hours, and a considerable pressure is developed. When the tube is placed in darkness the pressure decreases for some days and then remains constant. The pure acid stored in sealed tubes in darkness reaches the latter equilibrium in 6 to 12 months. The presence of water delays the process especially the spontaneous decomposition in darkness.

High Frequency Oscillations—X-Rays.

Kossel's theory of the mechanism of X-ray emission is founded on Bohr's planetary electron atom. He postulates that an inner electron is forced out of the atom either through absorption of high frequency X-rays, or by bombardment with high speed electrons. If the electron is forced out of the K level, K emission of X-radiation follows because the electron is replaced by another from an outer (L or M) level, the process of replacement constituting the emission. Similarly the replacement of an L level electron by one from the M or N levels entails L emission. No oscillatory process within the atom is depicted—the frequency of the emission depends on the nuclear charge, and the respective distances of the displaced and replacing planets.

This theory is concerned therefore with the displacements towards and away from the nucleus.

A different view of the connection between X-rays and electrons has been outlined above* ; according to this the radial shells, when a sufficient impetus is forthcoming, oscillate sharply towards and away from the nucleus, and in consequence of the very high elasticity in the direction of the nucleus the frequency of these vibrations greatly exceeds that of the electrons which have been displaced in the plane of the shells. The frequency of the characteristic $K\alpha$ radiation of sodium, for instance, is about 500 times that of the vibrations which are responsible for the sodium D lines.

Shells and their Frequencies.

A fundamental question that requires an answer is this—Are the frequencies of the lines in Barkla's K, L, M, etc., characteristic X-ray spectra to be associated with those of particular shells? If they are, is it possible to point to shells as being probably concerned with certain lines? In the case of sodium we may conjecture that the oscillations of the two potential valence shells give rise to the shorter $K\beta$ emission (using the notation employed by Siegbahn in his "Spectroscopy of X-rays"), those of the four radial paired shells being responsible for the lower frequency $K\alpha$ rays, and the $K\alpha$ absorption of De Broglie.

We assume that the frequency of both potential shells is the same, as is that of the four radial pairs.

If the orbits of the radial and potential valence systems did not mutually affect one another, the graphs of Moseley's relation for the K series would consist of two straight lines, but as the atoms become more complex, and the nuclear charge increases, some interference between the orbits occurs, and those of the two inner electrons become differentiated as do those of the radial shells, hence two $K\alpha$ and two $K\beta$ emissions are observed.

It is significant that when potassium is reached and four quartets replace the four pairs, they have no effect on the Moseley relation.

* P. 68.

The Barkla L emission commences with copper, the first element with a complete double radial system.

The four shells of the second radial system at first have presumably the same periodicity, since only one line, $L\alpha$ is observed, but as the nuclear charge, and structural complexity increase, slight differentiation becomes manifest here also.

The Significance of Ruthenium and Osmium.

In addition to the radial shells the position of the two further potential valence electrons has to be fixed. Now there is one circumstance which would appear to indicate what lines may be associated with these. In the reduced forms of the elements of the palladium and platinum families on p. 13, we have seen that the first members, *i.e.* ruthenium and osmium, *only possess the two potential valence electrons* of the K system. If, therefore, frequencies are to be associated with shells, no emission analogous to that from the L potential valence of other atoms can occur in the case of ruthenium and osmium. Reference to Siegbahn's Tables shows that these elements give no l and η emission of the L series, and we may conclude that the l and η emission probably has its origin in the second potential valence system.

The l frequency is the lowest of the L series, which indicates that this potential valence shell is situated farther from the nucleus than the rest. From rubidium to uranium the l line forms a straight line, so this shell appears to be free from external complications in the case of all atoms from 37 to 92.

The η potential valence electron at rubidium is the second farthest from the nucleus in the L series, but with increasing atomic number interference by other shells causes it to steadily approach the nucleus, and in the Rare Earths it passes inside the l shell. This circumstance must be intimately connected with the peculiar structure of the Rare Earths. That the orbits of the potential valence electrons and those of the shells outside them mutually affect each other was deduced from the study of chromophores in Chapter V.

There are two further points regarding potential valence electrons that X-ray spectra bring out :—

I. The l and η lines do not extend down to copper, the first element to contain these two extra electrons. Hence in the lighter atoms they may perhaps occupy a joint orbit or orbits, in a different position to that occupied in the more complex atoms.

II. Elements 45, 62, 66, 70, and 77 have only one l potential valence electron each (Chapter I.), but they show both l and η emission, a circumstance that indicates that the electron occupies the η position in some atoms of these elements, and the adjacent l in others.

Ionisation.

It is perhaps premature to assume that the electrons which are liberated when X-rays are absorbed are necessarily liberated from oscillating inner shells. They may be liberated from potential valence or valence shells nearer the exterior; the migratory tendencies of the former in chromophores have already been studied. The investigations of A. E. Lindh and S. K. Allison have proved that the X-ray absorption spectra of sulphur, phosphorus, chlorine, and silicon vary with the nature of the compounds in which these elements occur. Such variation is, of course, exactly what our study of the electron interpretation of oxidation and reduction lead us to expect. The presence or absence of latent valence pairs, which are probably closely related to the outermost potential valence electrons, may also affect the spectral lines of elements.

As X-ray technique improves, and diffraction means are devised between ruled gratings and the crystals at present employed, measurements of the longer rays emitted by the external shells of atoms will become available, and a fairly complete picture of atomic structure may be obtained.

Probably more reliable structural evidence will be forthcoming from X-ray research, than from the mathematical analysis of the high temperature spectra of stripped atoms, which seem likely to be of more immediate interest to the astronomer than the chemist and physicist. The results that have accrued already from the admirable work of Professor M. Siegbahn and his fellow workers on the X-ray

absorption spectra of the elements, lead us to hope that the various views that have been put forward regarding atomic structure may be sifted out before long. The evidence brought forward here, indicates that the state of oxidation and reduction of each element will have to be carefully considered in this connection. The fact that the curves of the "N" and "O" series show discontinuities and flattenings corresponding to the potential valence sections of the periodic system is very significant.

Meanwhile it will be convenient to keep the following points in mind in forming a provisional mental sketch of atomic structure; they are supplementary to the numerical data set out in Chapter I.

I. Barkla's K, L, M, N, and O series of characteristic X-ray spectra are connected with the 1st, 2nd, 3rd, 4th, and 5th radial systems, together with their associated potential valence systems.

II. The orbits of the first two potential valence electrons are rather nearer the nucleus than the first radial (K) shells, and give rise to the $K\beta$ emission.

III. The potential valence electrons of the second or L group revolve in separate orbits in most atoms. One of these orbits lies outside those of the second radial shells, and from rubidium onwards its relative position remains constant. The orbit of the other moves towards the nucleus relative to the other as the atomic number increases. These electrons are responsible for the l and η emission.

IV. The study of coloured cations indicates that the shape of the orbit of a potential valence electron is affected by the symmetrical or unsymmetrical distribution of shells outside it.

V. Electron magnetic shells possess *two* elasticities, that in the direction of the nucleus being higher than that in the plane of the shell, which is at right angles to the former. The former is chiefly, but not entirely, a function of the nuclear charge, and is concerned with high frequency oscillations, the latter depends largely on the mutual repulsion of neighbouring electrons, and is concerned with lower frequency phenomena.

VI. The orbits of spinning electrons consist of spirals about portions of surfaces that, like the earth's surface, are not truly spherical, since the spaces occupied by the K, L, etc., series are not bounded by true spheres because the potential valence systems must give rise to dissymmetry.

APPENDIX TO CHAPTER VI.

NOTE ON THE TEMPORARY ALTERATION OF ELECTRON ORBITS.

When a spring balance is depressed by the hand, and the latter is sharply withdrawn with a trigger-like action, the indicator comes to rest in the zero position after performing a few periodic vibrations.

If, however, the hand is more slowly withdrawn, little or no oscillatory movement may be observed.

Such a mechanical analogy may help one to understand why certain modes of disturbance of the normal movements of the electrons in their magnetic shells are associated with the emission of characteristic radiation, and others are not. During the thermal encounters between atoms, the somewhat slow rate at which their centres approach and recede will vary greatly with the temperature, state of combination and other circumstances, hence the magnetic motions caused by such encounters would correspond to the somewhat tardy withdrawal of the hand as above.

The collapse of an ionised shell is a trigger-like release phenomenon, an unrestricted process that gives rise to a short train of magnetic waves.

In general, the damping effects of the neighbouring shells of the same or of associated atoms, converts the periodic motion of an isolated shell (line spectrum) in simple cases into compound periodic motion (band spectrum), or into white light and radiant heat in more complex cases.

The X-ray motion of electron shells (especially the inner shells) towards the nucleus probably meets with high resistance, and unless a sharp blow is delivered, the nucleus itself recedes simultaneously. Even bombardment with high speed electrons allows time for measurable recoil (Compton effect).

CHAPTER VII.

THE STRUCTURE OF SOLID CONDUCTORS AND MAGNETS.

THE potential valence electrons are such active constituents of atoms in the chemical sense, that it is of interest to inquire what part they may play in physical phenomena. We have already seen that they are probably important factors in the mechanism of characteristic X-ray emission, and also in chromophores. We shall now consider certain aspects of conduction and magnetism.

The Crystalline Allotropic Varieties of Carbon.

Peculiar interest centres around the electron structure of graphite and diamond, because, among other things, the conductivity, opacity, and metallic lustre of the one, stand out in such sharp contrast to the resistivity and transparency of the other. Any conclusions that can be reached regarding the movements of electrons in them are therefore of importance, because they may throw light on the problems of metallic conduction, reflection, and absorption.

The oxidation products of graphite led chemists long ago to suspect that its atoms were united in a series of closed chains of six atoms.

The diamond is the hardest material known, and its atoms are the most closely packed of all the elements. If, for instance, the atoms of iron and platinum could replace those of carbon in the diamond, they would possess densities of 16.3 and 57.0 respectively.

The crystal structures of the diamond and graphite have been described by Sir Wm. Bragg in the volume already referred to, and a fuller account is given in "X-Rays and Crystal Structure," by Sir Wm. and Professor W. L. Bragg.

X-rays give information regarding the spacial distribution of atomic nuclei only—the electron distribution about these nuclei has to be inferred.

The diamond appears to be simply related to methane. If the tetrahedrally situated hydrogen atoms of methane were replaced by four methyl groups, and all the hydrogen atoms of the latter were similarly replaced by more methyl groups, and so on indefinitely, one would obtain a structure like that of the diamond, provided they were correctly spaced out, the atoms in every fourth row, instead of being over those in the first, like the oxygen atoms in ice, being situated between them, *i.e.* they are as far from each other as possible.

We assume that each carbon atom is connected tetrahedrally to four similar atoms by four heterovalent pairs of electrons, and that the atoms are in the state of basic activation described in Chapter IV., each having two potential valence electrons.

In graphite the carbon atoms are distributed hexagonally in sheets, the sheets being only very weakly connected to similar ones above and below.

Graphite appears to consist of a connected series of aromatic nuclei, but it must be noted that although all the hexagonal groupings behave alike to X-rays, there must be a very important difference between some of them. This structural difference corresponds to the well-known fact that although aromatic nuclei can be connected to form structures such as naphthalene, anthracene, and phenanthrene, ones of the type



are unknown.

Aromatic nuclei can only be connected in certain ways; there are not sufficient electrons available in some cases,

where every carbon has to be attached to three others, because to each must be allotted the latent valence pair which is the characteristic feature of aromatic carbon.

It is, however, possible to arrange aromatic nuclei in layers in such a manner that this difficulty is overcome, in fact it can be done in more than one way. The simplest manner is that depicted below. It may be termed the polyphenyl arrangement since every carbon atom of each aromatic group is connected to another aromatic group in diphenyl fashion.

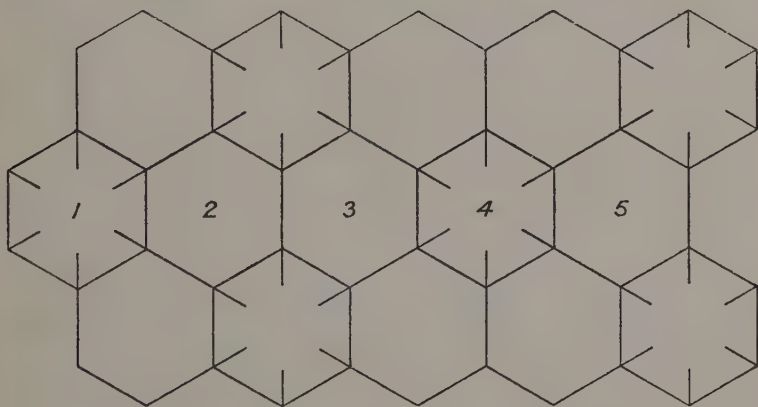


FIG. 5.

In this arrangement every carbon atom contains one potential valence electron. Every aromatic nucleus is surrounded by empty hexagonal spaces, and if parallel straight lines are drawn through the centres of the hexagons it will be noted that the aromatic nuclei occupy every third line, and two-thirds of the groupings are unoccupied by paired shells (p. 55).

The Conductivity of Graphite.

One can readily form a picture of the process of conduction when a charged body is brought into contact with a crystal of graphite. Since each atom has but one potential valence electron, an additional electron can pass into the potential valence system of the nearest carbon atom, and from

there it can pass into the next and so on. The migratory process is similar to that which occurs in chromophores, with this difference, in the latter the movements are confined to one or two atoms and are oscillatory in character—there is no ready passage from molecule to molecule. In graphite the molecule is indefinite, each crystal plane is one large molecule, and the electrons can continue the forward movement through millions of atoms since all are similar.

There is another important feature of the structure which may be connected with the metallic lustre and opacity of graphite. By a slight change of orientation of the latent

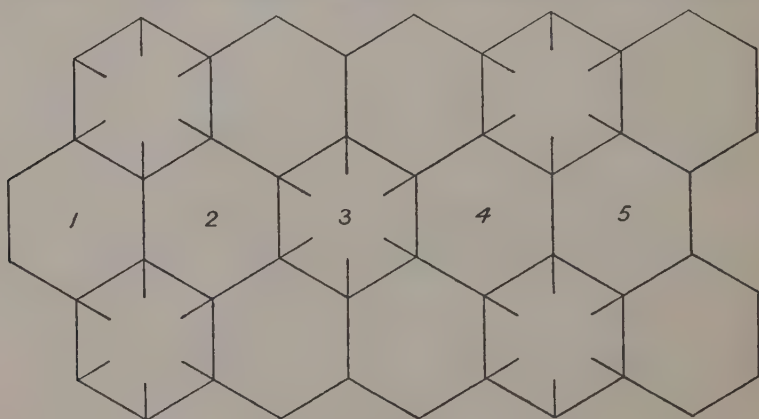


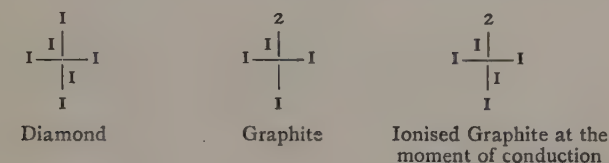
FIG. 6.

valence pairs, the aromatic groupings and the unoccupied spaces can be interchanged (compare Figs. 5 and 6).

Here one-third of the previously empty spaces have become aromatic nuclei, and as many aromatic nuclei are now replaced by unoccupied spaces. A mere sliding of the latent valence pairs around nuclei is all that is necessary to effect the change. Perhaps the play of forces is so finely balanced that the transformation is always proceeding, and in graphite, when illuminated, paired shells are continually undergoing reorientation, like weather-vanes on a boisterous day. Such movements enable them to absorb, or repeatedly reflect radiation over a very large range of frequencies, *i.e.* the material has the property of a black body; the millions

of *rotating* reflectors break up all incident radiation except that reflected from the external layer.

It is the presence of but one potential valence electron in the atoms of graphite that endows it with physical properties so entirely different from those of the diamond. In the latter electron migration between atom and atom cannot occur, the places of call are fully occupied, and re-orientation of shells is impossible; there are no latent valence pairs attached to the carbon atoms of the diamond, each atom is united to four others instead of three. The structure of the carbon atoms dissected out is as follows :—



Reduction.

We have defined active valence electrons as those which are common to the valence system of two atoms, and the reduced state as that in which there are the smallest number of active valence electrons (p. 34).

The liberation of an element from a compound is often described as one of reduction, but here we see that the active valence of the diamond is the same as that in methane or carbon tetrachloride, *i.e.* all the atoms are in the highest state of *basic* activation, and those of graphite are in the same (lower) state of basic activation as the carbon atoms in ethylene. Obviously a knowledge of the atomic associations of an element is required to enable us to say whether it is in a reduced state in the above sense.

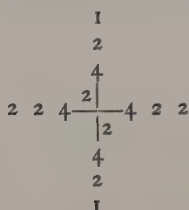
The Conductivity of Selenium.

When selenium, which has been kept dark, is exposed to light its conductivity increases. This reaches a new steady value after rather more than a minute's exposure. When the light is cut off the conductivity falls back to the original

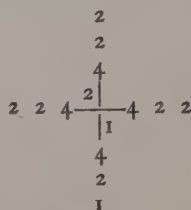
value. Again the period of variable conductivity occupies rather more than a minute.

Perhaps the light, as in the case of chromophores, forces one of the electrons from a potential valence position. The new atomic structure is then that of an electron receptor being analogous to that of the carbon atoms of graphite, and as all the atoms are similar, electrons can pass from one to another by way of the potential valence systems.

In terms of dissected atoms the molecules of the two forms of selenium may be built up of



A poor conductor.



A good conductor.

In the chromophore hypothesis of the passage of an electron from the potential valence system of one atom to that of the next, there are two atoms, the emitter and the receptor, in contact, and the latter certainly does not play an indifferent rôle. Organic chromophores are restricted to two *particular* atoms, the play of forces being such that each takes part in the transfer—there is a push and a pull as it were—there must be room for an electron in the potential valence system of the receptor. If we consider the superficial layer, for instance, there is no migration outwards because there are no receptors pulling. As soon as the forces of emission are sufficiently strong for it to eject electrons spontaneously, the body becomes self-luminous : shells are ionised and collapse again, and thermionic phenomena supervene. Perhaps the principal difference between organic and metallic chromophores is this—migration is localised in the former to a pair that are isolated from similar chromophores by atoms between which migration does not occur, hence the process is entirely oscillatory ; in the former the migratory process can proceed from atom to atom indefinitely in closed chains or

irregular open chains, since every atom has several neighbours that can act as receptors.

Some physicists have pictured electrons as moving about in conductors like the molecules in a perfect gas, and applying the laws of the kinetic theory, have calculated that they are moving with an average velocity, some sixty times that of the molecules in hydrogen gas.

The above considerations, if correct, considerably modify such a conception. The movements of free electrons may be limited to certain paths which can be distorted or interrupted by physical and mechanical treatment; the mobile electrons during conduction, unlike the molecules of a perfect gas, may be undergoing repeated association and dissociation of a particular type. If the electrons in conductors were "free," we should expect metals to be self-luminous, for the free electrons should ionise the valence shells, and the collapse of the latter would lead to the emission of radiation from the surface. This is the characteristic of bodies approaching red heat, when thermal agitation is sufficient to cause the separation of some of the valence pairs.

Temperature and Conduction.

Conductivity increases as the temperature falls, and reaches a maximum as absolute zero is approached. This, in terms of conduction by means of electrons migrating from one potential valence system to the next, may mean that the passage of electrons *by the shortest route* depends on all the surrounding atomic nuclei being the same distance apart. Thermal agitation causes irregularities in these distances, and deviations of the paths occur, the length of which increases as the temperature rises. Homogeneity of crystalline structure is essential to the development of the highest conductivity. The transference of potential valence electrons only occurs between atoms that are united by valence pairs perhaps, and whose nuclei are correctly spaced apart at the moment of migration. Liquefaction, therefore, lowers conductivity. Mercury offers a high resistance, *i.e.* 95×10^{-6} . Most alloys offer a rather high resistance also, and the cold

working of metals, which it is suggested below forces some of the atoms into cells surrounded by combined atoms, increases the density, resistance, and strain in metals, all of which are changed by heating.

Insulators.

The insulating properties of sulphur (Chapter III.) and paraffin wax depend on the stability of their fully occupied potential valence systems.

Metallic Conductivity.

Having examined the mechanism of the conductivity of graphite the question naturally arises—Is metallic conductivity analogous to that of graphite?

In dealing with this question it will be convenient to divide metals into two groups (1) the workable metals that are used in industry, whose external radial system consists of paired shells (p. 7), and (2) the metals of the alkalis and alkaline earths.

In the first instance it is apparent that neither the number of extra-nuclear electrons, the type of packing of the atoms in the crystals, the number of valence electrons, the chemical properties of the atoms, nor the density of the material, are the chief factors in conduction, as a comparison of the constants of a few whose resistivity is much the same shows.

Metal.	Atomic Number.	Density.	Packing.	Resistivity.
Lithium	3	534	Body centred cubic	8.4×10^{-6}
Iron	26	7.8	Body centred cubic	9×10^{-6}
Nickel	28	8.8	Face centred cubic	11.8×10^{-6}
Osmium	76	22.47	Hexagonal	9.5×10^{-6}
Platinum	78	21.45	Face centred cubic	11.0×10^{-6}

Metals as Chromophores.

Next we note that the light which is reflected from metallic surfaces is not polarised. Now this phenomenon is

characteristic of the surface colours organic chromophores—complex molecules which contain groupings connected by two atoms, whose potential valence systems very readily undergo changes which lead at times to the migration of an electron from the system of one to that of the other (see Chapter V.). All such migratory changes lead to temporary re-orientation of the paired shells surrounding the atomic nuclei in question, and we have seen that such re-orientation is probably characteristic of the carbon atoms in graphite. The fact that the radiation reflected from metallic conductors is non-polarised is therefore consistent with the migration of electrons from the potential valence system of one atom to the next, and re-orientation of paired shells about metallic nuclei. If paired electron shells reflect some of the radiation that impinges on them, the fact that they were *flickering or quivering, instead of steady*, would lead to irregular interference between the reflected units. This phase of the subject is discussed at the end of Chapter VIII.

A Second Mode of Conduction.

Now in the case of graphite we noted that there were insufficient electrons to convert all the hexagonal groupings at the same instant into aromatic nuclei, and concluded that the latent valence pairs were probably continually re-orientating. In metals a similar state of affairs may exist. Of the neighbours only a few may be combined with the central atom by paired shells at any moment, but by re-orientation of the latter the “bonds” may be shifted to another—in other words, a state of dissociation in the solid condition of a special and restricted type may exist. It is probable that paired shells, as in the case of single potential valence electrons, *are transferred from atom to atom*, like the baton in a relay race, and that a proportion of ionised atoms, akin to Arrhenius’ ions, exist in such metals.

The following diagrammatic representation of the process of re-orientation and the transfer of paired shells may be helpful.

The circles represent atoms, and the full line a paired shell uniting two of them. In the case of metals, the "bonds" after a circular movement (indicated by the arrows) connect a fresh pair of atoms (broken lines). By several repetitions paired shells can be transferred to distant positions.

Conduction by pairs may be the principal mechanism in certain cases such as the alkali metals.

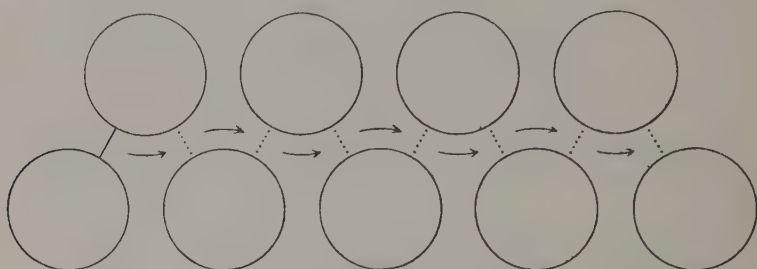


FIG. 7.

The Alkali Metals. Atomic Volume.

Hardness or close packing is characteristic of crystals which consist of atoms all of which are chemically united in three dimensions by paired electrons, as may be seen in the diamond, carborundum, and quartz. When these bonds are confined to two dimensions as in graphite, or the ties consist of the electrostatic forces between ions or of hydrogen nuclei balanced between other atoms, softer and more brittle crystals result with the atoms more widely separated.

The alkali metals are distinguished physically by their very high atomic volumes and softness, which stands out in sharp contrast to the smaller atomic volumes and much higher melting-points of the metals of the copper and zinc sub-groups.

A possible and simple explanation of this difference between the members of the sub-groups is concerned with the stability of their respective potential valence systems. The atoms of copper, silver, and gold in the metallic condition probably have their valence electrons augmented by others from their potential valence systems, and are thus enabled to form several paired valence "bonds" with other atoms,

hence their atoms pack fairly closely together in the crystals. The atoms of the alkali metals on the other hand, which only form one series of salts, may only possess their single valence electron, their potential valence systems being too stable to readily part with electrons. Such differences in stability may be concerned with the presence of radial pairs outside the quartets in the copper and zinc sub-groups (see Chapter I., p. 7).

Ions in Metals.

During the last forty years attention has been concentrated chiefly on the nature and properties of ions in solution—the ion as conceived of by Arrhenius to account for osmotic pressure phenomena, Faraday's electrolytic laws and other matters.

The ions of gases and solids have not yet received much chemical attention, although they are ripe for consideration. We have already referred to the chemical reasons advanced by Noyes as evidence for the presence of ions in the case of the halogens. The chromophoric character of the halogens supports his conclusion. In the case of solids, the disposition of the atoms in some crystal lattices is such that each atom is surrounded symmetrically and equidistantly by a number of others of a different kind; electrostatic forces might be expected to facilitate such a disposition. We must admit, therefore, that the crystals of certain haloid salts, oxides, and sulphides may be built up from ions.

The migration of electrons in certain chromophores results in the momentary formation of two ionised portions of the same molecule, or chemically united ions.*

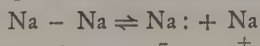
In the early days of Arrhenius' theory, many experienced difficulty in picturing the existence of differently charged kinetic constituents within a conducting medium, and at first sight the suggestion that certain crystalline metals may be built up of positive and negative ions may seem strange.

But we know now that the constituent parts of the atoms themselves are differently charged, and our conceptions of

* It would be convenient to employ some new term such as pro-ions, to distinguish ions (*i.e.* electrified constituents) which are united from those which behave like separate molecules.

"charged" bodies and their properties may yet have to undergo considerable further modification as will appear in Chapter VIII.

The body centre packing of the alkali metal crystals results in an extraordinarily light structure. Let us suppose that half the atoms give up their electrons to the other half,

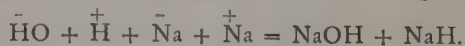


and that the positive ions are inside the cubic cells surrounded by the negative ions. In terms of layers, one layer is positive and the next negative. The atoms of the negative layer have now sufficient electrons to form a few pairs and unite amongst themselves to some extent, but as there are not sufficient paired shells to unite all the neighbours, the shells undergo continual re-orientation. On this view the lightness of the metals is due to the fact that the chief (but not the exclusive) force holding the atoms together, is the electrostatic charge of the ion.

But there are other considerations besides atomic valence which lend support to the ionic structure hypothesis.*

The Photoelectric Properties of the Alkali Metals.

The exceptional ease with which electrons are detached from the alkali metals by radiation is quite consistent with the existence of ions in the metals, for if potassium, for instance, contained ions, the negative ion would possess a paired shell in the valence position, and as it retains one electron more than its nuclear charge, such a shell unbalanced by others around the nucleus would be unstable and therefore readily disrupted by radiation, with emission of electrons. Again, it may be recalled that when the alkali metals re-act with water, *two* products are formed, alkali hydroxide and an explosive hydride. The reaction may be expressed by an equation similar to that which Noyes has employed for the reaction between the hydroxides and the halogens



Of the two methods of conduction—transference by electrons from one atom to another in chemical contact with

* See Appendix.

it, and the re-shuffling of paired shells, intact, from atom to atom—the first may be that which is responsible for currents through graphite, and the second for those passing through the alkali metals whose potential valence systems are too stable to be disturbed.

The Ferromagnetism of Iron and Heusler's Alloys.

The *external radial* system of the atoms of the workable metals, which are used in the various industries, consists of four paired shells (Chapter I., p. 7).

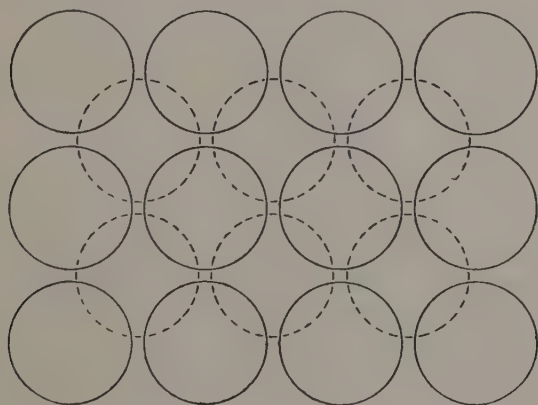


FIG. 8.

The crystals of all such metals may be supposed to be built up from sheets of atoms, each one atom thick. In the case of those metals whose atoms are arranged in face-centred cubes, such as nickel, copper, silver, gold, aluminium, iridium, and platinum, the atoms in the sheets are arranged in straight lines at right angles to one another (Fig. 8).

Those metals whose atoms are packed on the hexagonal plan, such as zinc, cadmium, and osmium have their atoms arranged in rows at angles of 60° to each other (Fig. 9).

In both cases the atoms in successive sheets are disposed over the spaces between the atoms in the sheet below, hence

the atoms in the third sheet are exactly over those in the first.*

The atoms in crystals of iron at temperatures above 900°C . are arranged in face-centered cubes, but during the phenomenon of recalescence, the atoms of the first and third sheet appear to be drawn together, and are probably chemically united, with the result that the atoms of the second sheet become disconnected, each atom of the second sheet becoming surrounded by a cell of eight other chemically united atoms. *Inside this shell it leads a more or less independent existence.*

The heat liberated during recalescence is a measure of the nett chemical changes during the re-arrangement.

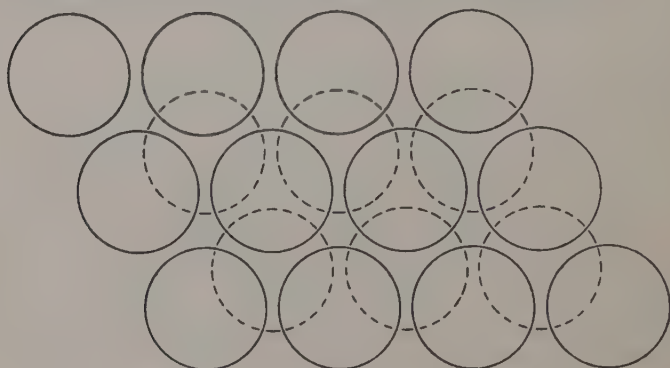


FIG. 9.

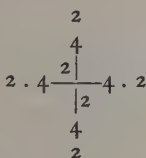
As there are an equal number of atoms in each sheet, during recalescence half the atoms form cells round and imprison, as it were, the other half.

The exceptional magnetic properties of iron are probably due to the fact that the enclosed atoms are able to rotate inside the cells, and become so orientated by external magnetic fields, that their own natural fields augment those of the external field, instead of mutually neutralising each other, "saturation" occurring when all the atoms are correctly aligned.

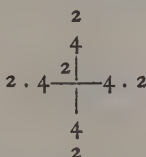
Attention has already been drawn in Chapter II. to the

* As viewed from another direction the atoms in every third layer appear to be over each other.

symmetrical structure of the important volatile compound of nickel $\text{Ni}(\text{CO})_4$. Since iron cobalt and nickel in their similar states only differ in the number of their potential valence electrons, if the atoms of nickel (28) have the structure (see p. 26)



those of the enclosed iron (26) may be represented by



As the encaged atoms have their freedom of movement impeded by (1) the eight surrounding atoms, (2) the six similarly encaged atoms in the six similar cells around them, it at all times requires the expenditure of work to align them in a definite direction, as distinct from the chance orientation they assume in consequence of thermal agitation, and the phenomena of hysteresis, which Sir Alfred Ewing's researches have revealed, may be ascribed to such resistance, the presence of small quantities of other substances such as cementite Fe_3C , considerably affecting this in steel.

Although a very large proportion of the magnetism of iron is due to the enclosed atoms, a small proportion must be ascribed to the enclosing cells, since the face-centered crystals of cobalt and nickel, although they do not possess the enclosures, exhibit feeble paramagnetism.

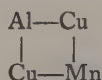
Heusler's Magnetic Alloys.

These appear to be closely connected with iron structurally. Two of them were examined by Mr. J. F. T. Young *

* *Phil. Mag.*, 1925, vi., xlv., 291.

in Professor McLennan's Laboratory at Toronto; their composition was not far removed from that required for the alloy $\text{Cu}_2 \text{ Al Mn}$, the composition of which is 60.7 per cent. Cu, 12.9 per cent. Al, 26.4 per cent. Mn, but both contained a slight excess of aluminium, *i.e.* 14.3 and 15.9 per cent.

If we assume that these three metals each retain two potential valence electrons in the metallic state, the four atoms $\text{Cu}_2 \text{ Al Mn}$ have altogether $11 + 11 + 3 + 7 = 32$ valence electrons, *i.e.* just the same number as four atoms of iron 4×8 . We may assume, therefore, that each sheet consists of squares arranged thus:—



connected by paired electrons.

Now Mr. Young, in his X-ray investigations of the structure of the alloys, found that the specimen which contained the higher proportion of aluminium consisted of mixed crystals, both body-centred and face-centred cubes being present, which points to the excess of aluminium being encaged as free atoms in cubic cells of eight chemically united atoms, as in the case of iron. This alloy possessed much more strongly marked ferromagnetic properties than the alloy with only 14.3 per cent. of aluminium which consisted of face-centred cubes.

The change in iron from face-centred to body-centred cubic packing is spontaneous, but a similar change, more or less complete, occurs when thin sheets of copper, aluminium, silver, or gold are hammered or rolled; the atoms of one sheet are strained apart and enclosed by those of the sheets above and below it, probably in a very irregular manner, for X-ray examination shows that the crystals are now heterogeneous. That many of the atoms are strained is apparent from the fact that on heating (annealing) the atoms in the crystals tend to return to the face-centred type of packing, and the foil becomes softer.

In the case of gold the strain is revealed by another

circumstance. The thinnest gold leaf is transparent and greenish light passes through.

Now the study of chromophores in Chapter V. led us to the conclusion that many of these possess groupings united by weak "bonds," which spontaneously undergo incipient or actual dissociation and reassociation. In the case of gold the chromophoric structure has probably been mechanically induced by strain; it may be of the type that was considered in the case of acridine, contiguous atoms being at one moment united by paired shells, and in the next dissociated. On heating the gold leaf the body-centred cubic packings and the chromophores are destroyed, and the gold changes colour.

There are features of packing of the atoms in the iron family, besides magnetism, that deserve attention.

The conception of close packed spheres in the case of metals, although useful up to a point, must not be carried too far. A sphere cannot be surrounded by eight others of the same size all of which are in contact with each other, *although the presence of slight projections on each, directed towards the neighbouring atoms, enables them to do so.* The valence pairs around atoms may in effect constitute such projections; models of body-centred cubes should be constructed with beads between the spheres to enable the cell to hold the encaged atoms.

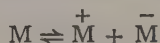
Attention is drawn here to the crystalline peculiarities of the different members of the same family. Although the members of the iron, palladium, and platinum families differ only in the number of their potential valence electrons, the members do not crystallise in the same manner. Thus ruthenium and osmium, which have only the two K potential valence electrons, are arranged in hexagonal packing, whilst nickel, rhodium, palladium, iridium, and platinum pack as face-centred cubes. Cobalt (like cerium) packs in both ways. It is probable that the distribution of the potential valence electrons influences that of the outer valence system, and hence the arrangement of the atoms in layers.

APPENDIX TO CHAPTER VII.

NOTE ON THE METAL-POTENTIAL SERIES.

In connection with the hypothesis of the existence of + and - ions in metals, it may be pointed out that this indicates an interesting modification of Nernst's theory of the metal-electrolyte potential series.

Nernst assumes that the metallic ions of the electrolyte are in equilibrium with the metallic electrode, in the manner that a vapour is in equilibrium with a liquid or solid. The equilibrium may be an indirect result, however, for if metals are ionised the fact may be expressed by the equation



and when + ions are present in the electrolyte at the surface of separation, the equilibrium is upset and electrons are set free.

Hence *vapour pressure need not be invoked.*

Assuming the more electropositive and photoelectrically active metals are more highly ionised than those at the mercury end of the scale, electrons tend to leave them more readily. Hence, considering a Daniell cell for instance, the zinc ions about the zinc surface cause a liberation of electrons which, when the external circuit is completed, pass by this to the copper (which is ionised to a smaller extent), the "conventional current" moving in the reverse direction. This hypothesis can, however, only be employed in conjunction with a full realisation of the part played by metal-hydrogen and metal-hydroxide surface effects. The phenomena of the dropping electrode and capillary electrometer prove that a fresh surface of pure mercury for instance, when exposed to air is covered by an almost invisible layer of hydroxide in less than one-hundredth of a second, and the high and variable figures obtained by several distinguished physicists for the surface tension of mercury are undoubtedly due to the fact that they were dealing with such films. The presence of oxidising and reducing agents in solution often modifies these effects in a remarkable manner.

CHAPTER VIII.

ELECTRONS, PROTONS, AND ETHER.

“ . . . tell me how an electrick Body can by friction emit an Exhalation so rare and subtle and yet so potent as by its Emission to cause no sensible Diminution of the weight of electrick Body—and yet to be able to agitate and carry up Leaf Copper or Leaf Gold at the distance of above a Foot from the electrick Body ? ”

—SIR ISAAC NEWTON, “OPTICKS,” *Query* 22.

WE have attempted to show in the previous chapters that behind the chemical phenomena known as oxidation and reduction, there are electron displacements and re-arrangements which affect a small group, which we have termed the potential valence system. Moreover, we have advanced reasons for believing that the anomalies connected with the periodic classification of the elements, the behaviour and properties of chromophoric groups, and the presence of certain features in characteristic X-ray spectra, are mainly dependent on the presence and movements of these electrons. Such considerations affect every branch of theoretical chemistry and important physical conceptions, but it seems unlikely that we shall make much progress in the further elucidation of these problems unless the relationships of electrons, protons, and ether are cleared up and developed.

The electrostatic anomaly of the Rutherford atom is the fact that the extranuclear electrons are not attracted towards the nucleus until they make contact, a circumstance which is probably connected with the magnetic forces associated with the spiral movements of protons and electrons. We shall, therefore, proceed to consider these forces in terms of ether.

The Ether.

The leading physicists of the world are sharply divided into two camps at the present time regarding the very

existence of the ether. One school maintains that we cannot explain any of the phenomena concerning radiation without reference to it as the medium of transmission, whilst others of the relativity school consider it an unnecessary conception. The following pronouncements may be taken as typical :—

“The most usual view of radiation is that it consists of waves in a connecting medium, commonly called ‘the ether,’ and that this same unique and only ether is responsible for gravitative attraction, for electric and magnetic attractions, and for cohesion : that is, for all the forces which tend to bring bodies together, while motion tends to keep them apart.

“The very fact that bodies separated in space attract each other shows that there must be some intervening mechanism or substance to account for what are called their fields of force, and this is clinched by finding that the intervening space is full of radiation. It is through, and by means of, radiation that we are acquainted with all the other worlds in the universe. . . . Thus, the physical universe contains not only protons and electrons, but also a connecting link, which for brevity is best called the ether ; while radiation is most conveniently thought of as a perturbation, or vibration, or tremor, or quiver in the ether, excited somehow by a corresponding movement in the protons or electrons themselves ” (Sir Oliver Lodge, “Phases of Science,” p. 4).

The views of those who would dispense with the ether are reflected in the following quotations from Dr. Jeans’ eighteenth Kelvin Memorial Lecture : “The development of the theory of relativity gave its deathblow to the old luminiferous ether of Lord Kelvin, Maxwell, and Faraday. The main result of this theory can be stated in the form that all the phenomena of Nature go on precisely as though there were no ether.”

“The luminiferous ether failed, partly because it left no room for gravitation, partly because its mechanism had to be supposed to be too elaborate for the facts to be explained.” Note, however, Dr. Jeans’ very significant admission which follows :—

“Although generalised geometry can predict and explain all the systems of forces of the universe, it has its limitations ; there are features of the actual universe before which it stands powerless. Nothing in geometry can explain the essential differences between positive and negative electricity, or the atomicity of electric charges, so that the whole inner structure of matter, including the whole of chemistry, would be outside the scope of our supposed geometer.”

As it is possible that this impasse is due to our faulty conceptions of the nature of the ether, we propose to examine two assumptions which are generally made regarding the ether :—

(1) That the ether is a homogeneous body (this is tacitly assumed by writers on the subject).

(2) That the ether is capable of transverse vibrations and that polarisation cannot be explained without recourse to them.

We shall endeavour to show that it is possible to devise an ether which can be made the basis of physical and chemical requirements if the above assumptions are dispensed with.

The Constituents of the Ether.

The chemistry of the ether has been neglected. It has been generally assumed that the ether consists of one constituent whereas, like our atmosphere, it may consist of a mixture of several which possess different properties.

By framing a simple hypothesis regarding the properties of but two of these constituents, it appears that explanations of some of the principal features of electricity, gravitation, magnetism, and radiation, can be advanced, and a tolerably clear picture of the simpler relationships between them can be obtained.

The Properties of Ether Particles.

Let us assume that the ether consists of at least two kinds of particles which, for convenience, we may term positive and negative particles, whose masses are of the same order—very small compared with that of the electron.

We assume that although these particles are far more numerous per unit volume than the molecules of gases obeying Avogadro's Law, yet in some respects they behave like the molecules of perfect gases. They undergo very rapid diffusion when separated, and exercise pressure on surfaces from which they rebound without loss of energy, but, of course, only half that pressure on surfaces at which they are absorbed. This latter circumstance may be a factor that has lain unsuspected behind many physical phenomena.

Now the peculiar properties which we assume to distinguish the particles are these—the positive particles are absorbed by electrons, and the negative by protons; the kinetic particles, which are not absorbed, are reflected or rebound, hence the pressure due to the latter is double that caused by the absorbed particles.

An Explanation of Electrostatic Repulsion and Attraction.

When the leaves of an electroscope diverge with a "positive charge" it seems obvious that particles must be bombarding the under surface, and maintaining a dynamic equilibrium against the downward bombardment of gravity. When the leaves diverge with a "negative charge" a similar equilibrium is reached—through the agency of different particles perhaps.

When two electrons are surrounded by both positive and negative particles, as each absorb the positive, some concentration of the negative particles around the electrons occur. This is, however, greatest in the space between them, to which each contributes, *i.e.* there is a larger proportion of reflected particles about the contiguous faces than around the remote, and repulsion occurs. A corresponding result is obtained in the case of two protons.

The leaves of an electroscope diverge therefore because there is a larger proportion of positive or negative particles between the leaves than there is on the remote sides, owing to the presence of an excess of protons or electrons on them. An abnormal amount of positive ether surrounds a body containing an excess of protons, and negative ether similarly

abounds in the neighbourhood of unbalanced electrons. When such "positively and negatively charged" bodies are brought near each other, the conditions in the space between them are normalised by diffusion, and the excess of reflected ether particles on the remote surfaces forces the two bodies towards each other. The ethereal interpretation of Gauss' well-known theorem—the total normal induction over a closed surface = $4\pi e$ —being, the total partial pressure of the excess of one kind of ether on a closed surface remains constant although its concentration diminishes as the surface expands.

According to this view the electron is not negative electricity itself. Its electrostatic properties are due to the presence of an excess of negative particles in its neighbourhood, which repel another electron but attract a proton.

It is hardly necessary to point out that the importance of Sir Joseph Thomson's epoch-making discovery of 1897 is in no sense diminished if we have to modify our ideas regarding the functions of electrons and protons.

Electricity and Apparent Electricity.

A consideration of the position from this standpoint shows that

I. Protons and electrons are not electricity, but are electrified to a constant amount by two kinds of ether.

This constant electrification is a dynamic equilibrium.

II. Electric force results when electrons or protons, or atomic associations of them, are bombarded by two kinds of ether particles, which are present in different proportions on opposite sides.

III. If electricity be defined as that which is responsible for electrostatic movements, then the two kinds of electricity are those constituents of the ether, whose presence in variable proportions about the different sides of protons and electrons gives rise to directed electrical movements. The existence of another factor—selective absorption—is, however, essential to the production of electrical manifestations.

If the proportions of the two kinds of electricity in the ether which is far removed from charged bodies, be regarded

as the normal condition of the ether, it will be convenient to refer to the separated excess of either variety in the neighbourhood of charged bodies as *apparent electricity*, as we are only conscious of the electrical properties of ether after it has been so separated.

It is convenient also to regard the *charge on a body* as the excess of protons or electrons on the body.

A little reflection will show that since electric intensity is proportional to the rate of change of potential, this is equivalent to saying it is proportional to the rate of change of concentration of apparent electricity, or expressing it mathematically

$$\text{Intensity} = \frac{dv}{ds} = \frac{dc}{ds}$$

(v = potential, c = concentration).

For where there are no Faraday tubes of electrostatic force, the concentration of apparent electricity is either uniform (as it is inside a closed charged conductor) or it is zero, *i.e.* the ether is normal.

Free v. Restricted Absorption.

The “compounds” proton—negative ether and electron—positive ether are not apparent. They appear to be the simplest known synthetic bodies.

Radio-active phenomena have familiarised us with changes involving enormous transfers of energy, during the breaking down of atoms, spread over immense periods. Possibly *equally slow synthetic forces are at work.*

It may be recalled here that the mass of the hydrogen nucleus exceeds that of the protons in oxygen atoms in the ratio 1.008 : 1. Assuming that the mass of both is partly due to the absorption product, it is possible to advance an explanation of this difference.

The nuclei of all atoms except hydrogen contain several closely packed protons, which must mutually throw “absorption shadows” and “partially eclipse” each other, hence the absorption of negative ether may be somewhat retarded in the case of closely packed protons, as compared with the rate at which it accumulates when each is isolated.

The beautiful researches of Dr. F. W. Aston (Bakerian Lecture, P.R.S., 1927, A. 115, p. 487) have recently revealed the fact that the mass of the protons of the elements whose atoms are lighter than oxygen, also exceeds that of the oxygen protons very slightly, whilst those of the more complex atoms are, in general, very slightly lighter.

One might speculate that since electrons and protons spin in opposite directions, perhaps the original structures, millions of years ago, were dextro and lævo forms of similar figures, and the extra mass of the protons indicates that the negative particles, which they absorb, are heavier than the positive.

Mass Variable ?

Many physicists have assumed that m is variable since the ratio $\frac{e}{m}$ has been shown to be a function of velocity.

The above considerations indicate e as the variable. For the electrostatic charge is a diffusion property, and at speeds comparable with the velocity of light, time may be an important factor, and the concentration of negative electricity around an electron may be less than normal.

When an insulated body is suddenly electrified, the interval which elapses before the electricity affects another distant body separated by air, depends on the rate of diffusion of the rebounding electricity.

Gravitation.

In the case of a body absorbing kinetic particles uniformly distributed around it, the steady rate of flow of the particles towards the body, across unit areas of imaginary shells surrounding it, will vary inversely as the square of the radius of the shells. For whilst N particles have passed through a shell of radius 1, the same number have crossed through a shell of radius 2, and the numbers per unit area are

$$\frac{N}{4\pi 1^2} : \frac{N}{4\pi 2^2}$$

The effect of absorption, therefore, like that of gravitation, varies inversely as the square of the distance from the body.

If absorption is proceeding in all massive bodies there must be a continuous inrush of the particles from all sides towards them. These currents are not, however, symmetrical, in the case of neighbouring masses, because they mutually interfere with, and cut off part of each other's supply. Consequently the concentration of the particles between masses is slightly lower than that in free space, and the pressure of kinetic particles on contiguous masses tends to force them together.

Gravitation may, therefore, be due to the absorption of

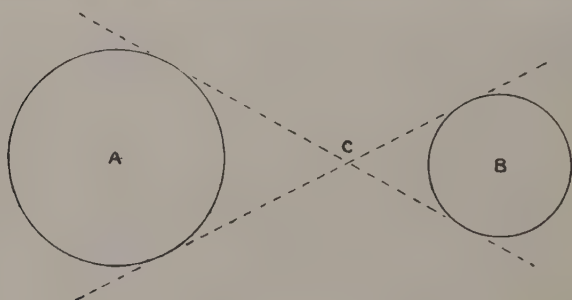


FIG. 10.

ether particles by the electrons and protons of which molecules are formed. It would appear to be permissible to regard this absorption mathematically, as negative radiation, and draw the following comparison when considering two bodies.

If A and B (Fig. 10) are two spheres of the same temperature, then by Prevost's theory of exchanges, the radiation received by A from B, and that by B from A are equal when equilibrium has been established. Hence C may be regarded as the source of the emitted radiation received by both. In the case of absorption C is the seat of absorption towards which each are equally forced.

The radiation transmitted from distant bodies to the earth must be affected by the ether currents towards massive

bodies, such as the sun, when their orbs almost intervene. This subject has, of course, been much discussed in connection with Professor Einstein's theory of relativity.

This picture of the function of the ether in gravitation is probably (in terms of protons and electrons) very similar to that finally envisaged by Sir Isaac Newton, as the following extracts from the "Opticks," 2nd English Edition, 1718, indicate :—*

"Query 19. . . . And is not the density thereof greater in free and open Spaces void of Air and other grosser Bodies than within the Pores of Water, Glass, Crystal, Gems, and other compact bodies? For when Light passes through Glass or Crystal and falling very obliquely upon the farther Surface thereof is totally reflected, the total Reflexion ought to proceed rather from the density and vigour of the Medium without and beyond the Glass than from the rarity and weakness thereof."

"Query 20. . . . Doth not this Æthereal Medium in passing out of Water, Glass, Crystal, and other compact and dense bodies into empty Spaces grow denser and denser by degrees . . . ? And does not the gradual condensation of this Medium extend to some distance from the Bodies and thereby cause the Inflections of the rays of Light which pass by the edges of dense Bodies, at some distance from the bodies? "

"Query 21. . . . For if this medium be rarer within the Sun's Body than at its surface . . . I see no reason why the increase should stop anywhere, and not rather be continued through all distances from the Sun to Saturn and beyond . . . if the elastick force of this Medium be exceedingly great it may suffice to impel Bodies from the denser parts of the Medium towards the rarer with all that power we call Gravity."

The opposite view has been entertained by many physicists during the past century; compare for instance Tyndall's language in his "Lectures on Light": "The waves pass from the rare ether of the air into the dense ether of the glass."

* Only queries 1 to 16 appeared in the first edition in 1704.

Magnetism.

Magnetic phenomena are not concerned with the separation of the constituents of the ether. The intervention of an earthed sheet of copper between magnets or magnetic shells, although capable of cutting off electrical effects, has but a negligible effect on magnetic forces.

In magnetism the constituents of the ether must therefore be regarded as moving, either in a mixed current, or as streaming in opposite directions like the ions in electrolysis. Now the latter conception leads to such difficulties in connection with the mode of propagation that it appears highly improbable, and the former alone appears compatible with observed phenomena.

The magnetic properties of wires conveying electric currents indicate that the ether is flowing round the wire, and therefore along the axis in the case of a solenoid. Faraday's "tubes of force" on this hypothesis correspond to "currents of ether." The circular rotation of the ether around moving electrons and protons can be most readily accounted for by assuming that the latter are unsymmetrical structures of such a character that they must necessarily spin or rotate as they move forward; conversely any ether movements which cause electrons to spin, compel them to move *in a definite direction*—a circumstance which underlies induced current phenomena.

Flying electrons must therefore be likened to rifle bullets rather than round shot. Like children's toy paper windmills, the faster they move the more quickly they spin.*

When a current travels in series through tubes containing solutions of (1) potash; (2) potassium chloride; (3) Hydrochloric acid, and (4) a wire, the magnetic effects at equal distances from the current are the same throughout, in spite of the very different modes of conveyance of the current.

* Spinning or gyroscopic movements of electrons were first discussed by Parson (Smithsonian Miscellaneous Collections, 1915), and Compton (Journal Franklin Institute, 1921, August, p. 145), the latter seeing in the electron the ultimate magnetic particle.

This fact indicates that electrons and protons revolve in opposite directions when moving forward ; electrons are magnetically equivalent to protons moving in the opposite direction. Were it not for the compensating effect of the magnetic fields around moving protons, it is probable that enormous magnetic fields would accompany falling and moving bodies generally.

The Magnetic Fields in Atoms.

Protons and electrons spinning whilst moving in circular or elliptic orbits constitute magnetic shells. A proton shell rotating in the same direction as an electron shell, about a common axis, would be repelled magnetically, although attracted electrostatically. Neither protons nor electrons move in straight lines, but in spirals, and as they approach each other the angles between their paths, which are negligible at a distance, become steeper and steeper until ultimately magnetic repulsion balances electrostatic attraction, and they move in nearly parallel orbits.

The magnetic repulsion between proton and electron shells affords the simplest explanation of the distance of the extra nuclear electrons from the nuclei of atoms.

The protons in atomic nuclei may be grouped in shells containing several of the former rotating in a small common orbit, whose magnetic field is opposed to that of the extra nuclear electron shells. There is indeed one circumstance which suggests similarities between the grouping of the radial shells of the Rare Earths (Chapter I.), and those of the protons in the nuclei of the radio active elements, for if the Table of Rare Earths, Chapter I., p. 15, is examined, in the order of diminishing atomic numbers, it will be noted that as we pass from family to family, a radial shell of four electrons is discarded each time, until four shells each containing four electrons have been dropped ; similarly in the passage from uranium to lead in the radio active series, at successive stages α particles each containing four protons are discarded.

Moreover, there are molecular considerations as well as atomic that point to the existence of magnetic fields about

nuclei. Consider, for instance, the liquefaction of a hydrocarbon vapour such as that of Hexane C_6H_{14} . The molecules are surrounded by hydrogen nuclei, which electrostatically repel each other. But the hydrocarbon is readily liquefied; there must, therefore, be attractive centres on the molecules or they would refuse to associate. If some of the hydrogen nuclei form one type of magnetic shell, and the remainder the other variety, the dissimilar shells on each will tend to associate, forming, perhaps, paired nuclear shells analogous to the paired electron shells situated between the carbon nuclei and themselves.

Induced Electric Currents.

When the ethereal rotation originating in a wire conveying a current spreads to and reaches the loosely attached electrons in a neighbouring parallel wire, it strikes the near side of these asymmetric structures first, and sets up a rotation of the electron *in the reverse direction*; this forces the electrons along the wire in the opposite direction to those moving forward in the primary. After the first contact the ether stream surrounds the electrons in the secondary, and directive impulses cease.

When the "current" in the primary ceases the ethereal rotation first ceases around that wire, the new conditions spreading outwards, hence the encircling stream acts momentarily on the far side of the electrons in the secondary after it has ceased on the near side, and an induced current is set up in the same direction as that in the primary before the "break" occurred. Lenz's law can, therefore, be readily interpreted in terms of rotating ether and spinning electrons.

Heat.

Heat appears when atoms encounter one another, either singly or in groups. After such encounters the atoms may or may not remain associated together. When the motion of matter is arrested, the ether moving with the latter *sets up momentarily electro-magnetic disturbances* among the

electrons and protons, *analogous to induced currents*, and the latter affect the kinetic energy of the atoms. The ether motion which results from the reaction between the atoms and ether during the encounter, may all be absorbed by neighbouring atoms (in which case local rise of temperature occurs, as when a bullet becomes embedded in a sand-bag), or, as in most combustion processes for instance, part of it travelling as ether motion through space, may raise the temperature of more distant bodies when the ether motion is absorbed by them.

At absolute zero encounters no longer occur, since kinetic movements of translation have ceased, and the spontaneous production of heat by extra-nuclear processes comes to an end. We have no right to assume that all ether thermal motion is periodic in character.

Diamagnetism.

If the magnetic flow of ether on passing through any material orientates some of the shells so that the natural flow through the latter supplements that of the field, the body will exhibit paramagnetism.

If, however, the magnetic flow is merely retarded on passing through a substance, the latter will naturally tend to move if free to do so, and will dispose as much of its mass as possible in the weaker parts of the stream, in other words it will exhibit diamagnetism.

If the resistance to magnetic flow is measurable, information concerning its direction should be obtainable from the study of the behaviour of spheres of diamagnetic bodies in powerful fields.

The Nature of Radiation.

Unless present-day estimates regarding the relative volumes of protons and electrons in atoms are hopelessly inaccurate, such phenomena as the total reflection of light from solid surfaces must result from reaction, which occurs, not at the surface of the protons and electrons themselves, but from surfaces of discontinuity in the ether surrounding them.

It is therefore important that we should ascertain, if possible, what is the character of this surface of discontinuity, and how the ether is distributed within material bodies, since the optical behaviour of all media depend on these conditions.

The most remarkable property of ether as we have depicted it, is the absorption of its constituents at the surface of electrons and protons on which all electrical and gravitation phenomena depend. If these have been correctly interpreted it will follow that the constituents diffuse into one another at an enormous rate when separated.

Such an ether is, of course, quite incapable of transverse vibrations and the only form of wave motion that can be associated with it, is that connected with compressions and rarefactions, as in the case of gases.

Radiation an Alternating Magnetic Disturbance.

Further, these ethereal waves have a definite physical character—they are entirely magnetic.

The compression in a wave-front constitutes a momentary stream of mixed ether advancing from the source; such streams as we have seen constitute magnetism.

The ether in the rarefactions which follow the compressions is perhaps in much the same condition as that in diamagnetic bodies placed in magnetic fields.

Quite apart from the mode of vibration, such a picture differs from that painted by Clerk Maxwell in this respect. There is nothing electric about the ethereal waves as they pass across free space; it is only when they come into contact with matter that electric displacements can be detected—at right angles to the direction of propagation.

We must remember that Maxwell's theory was framed to account for the ethereal properties of solid and liquid media; he co-related the dielectric constants and magnetic permeabilities of these, but it does not follow that his equations apply without due physical interpretation to *free space*.

It will be observed that Time enters as a factor here into three phenomena in very different ways :—

- I. The time required for an electric charge acting across air on another body—this is a question of diffusion rates.
- II. The time required for a magnet to react across air on another magnet—this is a question of the movements of streams of ether.
- III. The time required for radiation to pass across air from one point to another.

The first and second have no sharp beginning and ending—equilibria are gradually established. The third proceeds at a definite uniform velocity.

Briefly the theoretical position as regards Radiation at the present time is this :—

Newton's emission theory, which had been discredited for more than a century, has in recent times been shown to be more in accordance with photoelectric phenomena than the wave theory of Huygens, Young and Fresnel. The latter was accepted chiefly because it afforded an explanation of interference, and was in agreement with experimental evidence bearing on the velocity of the transmission of light through solid and liquid media. The introduction, however, of transverse vibrations of ether, which was made in order to account for polarisation, has not proved a satisfactory one. In spite of numerous attempts, no one has been able to devise an ether, solid or fluid, which fulfilled this office.*

What is wanted then is an ether transmitting waves consisting of rarefactions and compressions, radiation proceeding in limited bundles, corresponding to Newton's emitted particles, and an explanation of the polarised condition that can be imposed on such radiation.

This problem may not prove impossible of solution, for there are features of it discernible now which were never presented to Thomas Young and Augustin Fresnel; these great investigators could not visualise matter as it has been analysed by Sir J. J. Thompson and Sir E. Rutherford.

* An admirable exposition of this subject, in a lecture at the R.I. by the late Prof. H. A. Lorentz, appeared in "Nature," April 26th, 1924, p. 608.

Polarisation.

Now, it can, we think, be demonstrated that ethereal waves of compression and rarefaction, analogous to those of sound in air, may give rise to polarisation phenomena, and transmit limited bundles of radiation, surrounded by dark spaces, and we shall show that the necessary conditions, although at first sight they may seem wholly academic, may indeed be those which actually prevail in certain cases.

Let the "A's" in the diagram represent coplanar centres a few Ångström units apart, emitting monochromatic waves of compression and rarefaction all in the same phase, and let the "B's" stand for similar sources which differ by half a wave-length from the "A's" in phase.

A	A	A	A
B	B	B	B
A	A	A	A
B	B	B	B
A	A	A	A

The radiation emitted by such a system would be polarised, for interference would prevent the waves from spreading sideways, and it would be confined to thin layers containing the "A's" and "B's" respectively separated by dark layers. As the waves in each "A" layer spread out, interference between successive "A's" would lead to bright and dark bands within the layers themselves.

If a "B" is now placed between each "A" it will be obvious that pencils of light would result, which would proceed somewhat like simultaneous flights of arrows, if the radiation were restricted to short bursts, of some few hundred waves each followed at intervals by further bursts.

We will now examine a reflecting surface and see how far it reproduces the above features.

The Two Modes of Reflection.

Sound waves can be reflected in two ways. Compressions, for instance, are reflected from the closed end of an organ pipe as compressions, and rarefactions as rarefactions ;

on the other hand, at the open end of the pipe compressions are reflected as rarefactions and *vice versa*.

It has long been recognised that the phenomena of interference, concerned in the production of Newton's rings, prove that light waves when impinging on surfaces change phase or gain half a wave-length, under certain circumstances.

But two assumptions have been made in this connection which require revision in the light of atomic structure and ether, as depicted here, and it then appears possible to account for polarisation in terms of longitudinal waves. As diffraction and the rectilinear propagation of light can also be readily explained by these waves, it is therefore possible to eliminate transverse ethereal vibrations altogether. The assumptions are :—

- I. That the change of phase of Newton's rings occurs as the waves pass from the supposedly dense ether of the glass into the rare ether of the air.
- II. That the density of the ether at the surface of glass is uniform.

As regards the first the rings are of course as readily explained on the hypothesis that the change of phase occurs as the waves leave the dense ether of the air and enter the rare ether of the glass.

As to the second, the surface of a solid medium if sufficiently magnified would appear highly complex in even the simplest cases, the atomic nuclei being distributed according to its chemical composition, crystalline character, and so forth. For present purposes, however, we can regard the surface as far as the ether is concerned as divided into *nuclear* and *circumnuclear areas*.

Now the density of the ether around the nuclei—which contain all the protons and about half the electrons—is a minimum according to the ether absorption view, and the density in the circumnuclear areas is much greater and but little rarer than the ether outside. When, therefore, light waves break on solid media they react on a variegated ethereal surface consisting of rare nuclear ether and denser surrounding areas. At the former they may change phase, and at the latter retain it, so that the reflected or refracted

wave-fronts contain elements half a wave different from the rest.

Hence the nuclear areas are the ethereal analogues of the ends of open organ pipes in acoustics, and the circum-nuclear areas correspond to the ends of the closed organ pipes which reflect sound waves without change of phase.

The plane wave-front of a train of waves is in general no longer homogeneous after reflection. At the polarising angle the reflected beam is broken up into parallel layers or pencils, or rather, perhaps, short successive trains of parallel layers, if a beam of light consists of innumerable short trains of waves, due to the limited emission from each collapsing ionised shell. It will, therefore, be seen that the reaction between a plane wave and a reflecting surface may reproduce just those conditions which we have outlined as those in which longitudinal waves would transmit radiation of the nature of polarised light. The distribution of the interfering layers depending on the shape of the incident wave-front and that of the reflecting surface.

Parallel layers would result from the reaction between a plane wave and a plane surface, but the layers would spread fanwise when the light from a near point was reflected from a plane surface, *i.e.* they would spread as from a virtual image behind the plane.

Non-Polarising Surfaces.

The picture of a polarising surface which has just been outlined, presupposes only slow disturbing movements of the ether in the nuclear and circumnuclear areas during the time required for the reflection of each train of waves.

In the case of metals whose surfaces do not reflect polarised light, the swinging movement of the valence pairs around nuclear pivots, which has been discussed in Chapter VII., appears to be so rapid that the ether in the circum-nuclear areas is always in a "stormy" condition, and hence polarised layers are not formed.

The surface colour of the crystals of dyes (see Chapter VI.) being re-emitted by the vibrating shells, is not in phase with incident radiation, and is therefore not polarised. In

view of these considerations it is advisable that the polarisation characteristics of the radiation employed in photoelectric measurements, should be as carefully scrutinised as its frequency.

It will be observed that there is a fundamental difference of view-point regarding the relations between matter and ether waves here, and those which were envisaged during the last century. Here the vibrations are longitudinal, but, being magnetic, they react on electrified electrons and protons at right angles to their direction of propagation. Previously the vibrations were held to be *transverse* and they reacted directly on matter.

Refraction.

The velocity of transmission of sound through air is affected by currents of air. So also in discussing the velocity of light through media the presence of streams of ether must be taken into consideration.

All the electron shells surrounding nuclei act like centrifugal fans forcing (magnetic) streams of ether in definite directions ; vibrations traversing the orientated ether permeating transparent matter must have the paths of the particles moving in a direction parallel to the wave-front increased. *This increase may constitute the chief cause of the diminished velocity of waves through the material.*

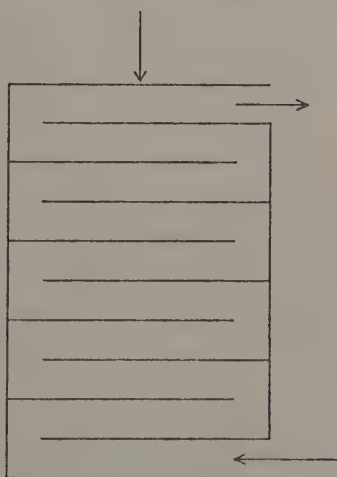


FIG. 11.

Currents normal to the wave-front would neutralise each other's effects.

The influence of the cross currents of ether in lengthening the path of the waves, might be increased artificially by passing them through streams of water ; if a sufficiently

rapid flow could be forced through an arrangement of the type shown in Fig. 11, the refractive index of water should be appreciably increased.*

The Dielectric Constant.

When a solid or liquid dielectric is interposed between two charged bodies, the rate at which the reflected particles of electricity previously diffused away from the respective contiguous surfaces is slowed down by the increased magnetic counter currents.

Hence in the case of each body, the concentration of the separated electricity about their contiguous surfaces tends to become more uniform as the result of the introduction of the dielectric, and therefore the electric force between them diminishes.

Although the effect of magnetic currents on wave motion and on diffusion phenomena are not strictly comparable, yet here, as in the case of Maxwell's theory, there is a close connection between the refractive index and the dielectric constant of a substance.

As is well known, the determination of comparable dielectric constants and refractive indices is a matter of great practical difficulty. Adsorbed surface films of moisture on solids are apt to cause disturbances—perhaps only absolutely dry conditions of Bakerian completeness should be employed—and liquids such as water allow some actual electrical separation to occur.

It will now be evident that although transverse vibrations cannot be impressed on ether in free space, nevertheless the magnetic currents in atoms superimpose transverse motion on waves of compression and rarefaction, and on diffusion currents, as they pass through optical media and dielectrics, and delay the transmission.

Dispersion.

When the effect of the lateral streams of ether on waves of compression and rarefaction is considered, the number of

* Bi-refraction in crystals arises through the magnetic currents between the layers containing certain atoms being stronger than others.

nodes and ventral segments in a train of waves per unit of length, is an important factor.

At ventral segments, where the displacements are greatest, there is least time for lateral displacements to operate, at the nodes there is much greater lateral displacement. The greater the number of nodes, the larger the integral of the lateral displacements; in other words, the particles in short waves, *traverse longer paths* in solid and liquid media than those of long ones, and have therefore a higher refractive index.

Sir Isaac Newton's Optical Views.

If we replace the Newtonian term "corpuscles" by "short isolated trains of waves" it will be seen that the great President's picture of the nature of light was in many ways akin to that just outlined. Even his ideas about "fits of easy reflection and transmission" have their counterpart in those we have outlined, concerning the conditions under which half a wave-length is lost when waves impinge on surfaces.

Photo-electric Phenomena.

Fluorescence and photo-electric emission appear to be closely related. In the former, radiation, whose frequency exceeds a certain limit, forces an electron out of one atom, but owing to the fact that there is another atom next to it which can act as receptor, it merely ionises one of its neighbour's shells, the latter becoming an emitter.

In photo-electric emission, the disturbed electron is free to leave the surface, or at least it can do so under certain circumstances.

When periodic disturbances are widely separated, the effect of each may be dissipated before the next arrives. It is only when the disturbances follow each other at sufficiently short intervals that their effects accumulate, and the nett result is integrated, a whole train or quanta is accepted, and violent reaction follows—the frequency of the incident

radiation must therefore reach a certain minimum to bring about a change in the system.

When electrons migrate under the influence of radiation, they may enter the potential valence system of an atom if there is room, as in activation (oxidation) and chromophores, or they may move around nuclei, or escape into space, as in the ionisation of gases and surfaces.

If the potential valence systems are already fully occupied, the chances of escape are increased, and this may largely account for the great photo-electric activity of the alkali metals (see Chapter VII.).

The photo-electric activity of radiation and its frequency may perhaps be connected as follows, taking as an example the red and violet waves in a beam of white light. If the trains of waves from the corresponding collapsed electron shells (Chapter VI.) were of the same length, say 100 cm. each, they would not contain the same number of compressions.

The violet train would contain about twice as many as the red. Now just as refraction increases with the number of nodes per unit length, so the photoelectric activity of light which exceeds the necessary minimum frequency, may depend on the number of ventral segments in each train.

There are, however, two features of the collapsing electron shells which must affect the nature of the resulting emission.

(1) There are *two* electrons left in the vibrating shells of the Balmer series, and the oscillations of these must interfere. The energy is not uniformly transmitted outwards, there are tracks whose amplitude is double that which either electron would produce, separated by dark tracks.

(2) The nature of the collapse suggests that the *amplitude* of the violet rays may be greater than that of the red.

Curves compiled from data regarding the heating effect of the rays in the different parts of spectra, should perhaps be analysed into two curves; one showing the number of trains of vibrations received, and a second the efficiency of each train. The maxima of such curves in the infra red

may be chiefly due to the enormous number of trains of long wave-length but low efficiency.

Relativity.

As physicists and mathematicians failed to explain the Michelson experiments, which appeared to indicate that the earth and its ether formed a single unit in the optical sense—the ether moving *with* the earth rather than *through* it—relativity was introduced as an ingenious way of overcoming the difficulty.

The Special Theory of Relativity.

The views that have been advanced regarding the nature of radiation cannot be reconciled with Professor Einstein's postulate regarding the invariable velocity of light.

Gravitation depends on the variable density of the ether in different places. It may be objected that the velocity of sound is independent of the barometric pressure. True, but the absorption of ether by matter gives rise to *currents of ether*. As the main current towards the earth is normal to its surface (or very nearly so as Foucault's pendulum experiment proves) we should not expect light to travel at different velocities in various horizontal directions at any given place on its surface. This conclusion agrees with the Michelson results.

The Velocity of Light and Ether Currents.

To detect ether streams directed towards the earth, by measurements of the velocity of light, by any ideal method, we should measure the velocity in *both directions separately*. Unfortunately, the experimental measurements only give the *mean of the two*. A beam of light departs and is reflected back again. Now we do not infer that a cyclist who takes two hours over a return journey takes one hour with and one hour against the wind, nor does a return echo travel at the same rate with and against the wind.

Ether Cross Currents.

A ray of light cannot travel in a perfectly straight line as it grazes a celestial body on its way to the earth. The path must be slightly displaced by the current of ether streaming towards the former—*Gravitational aberration* supervenes, although this is very minute.

Under certain conditions it might even be possible for one star to pass immediately behind another without suffering eclipse.

The apparent loss of velocity of light, in traversing liquid and solid media, was attributed above to the innumerable cross currents that deflect the ether, and lengthen the path of the rays, rather than to the change of density of the ether.

Gravitational aberration is therefore the simplest (one direction) case of refraction.

The General Theory of Relativity.

Turning to the general theory of relativity one feels inclined to put these questions to its adherents. Have you not in assuming you can dispense with the ether blindfolded yourselves? Can you ever hope to co-ordinate electricity, magnetism, and the structure of matter without it? Have you not, like the ancient Greek philosophers when their systems were threatened with checkmate, resorted to plausible *metaphysical* explanations, in preference to re-examining your difficulties through fresh physical spectacles?

One can imagine a race of intelligent beings, with no knowledge of molecular kinetics, working out many data by studying sound, physically and mathematically.

Having found they could predict certain phenomena and results, they might conclude that they could dispense with any theory concerning the presence of particles in air; but they would inevitably limit their horizon by such a decision!

The plane surface of space-time when this is far removed from matter (and absorption), can obviously be interpreted

in terms of the present outlook, with ether of uniform concentration : the curved space-time in the neighbourhood of matter, corresponding to ether of variable concentration, due to the operation of absorption.

As our ideas concerning the nature and relationships of ether and matter broaden, relativity may receive a new interpretation. At present we must try and appraise aberrations correctly ; when this is accomplished we may find Newtonian mechanics and Euclidean geometry sufficient.

We do greater honour to the illustrious investigators of the past by dissecting and reconstructing their views, than by labelling them "classical theories." The most urgent and important task confronting science to-day, is the revision of the physical assumptions which underlie the mathematical deductions of Fresnel and Clerk Maxwell in optics—wireless developments notwithstanding.

We shall assuredly have to draw still further on our *imaginations* if we are to succeed in extending Newtonian mechanics to the infinitely small, and account for the more important properties of ether and matter. Only then shall we consolidate the foundations on which to erect a structure worthy of the scientific discoveries of W. C. Rontgen, Sir J. J. Thompson, the Curries, and Sir E. Rutherford. ?

Here we conclude that the ether consists—in part at least—of positive and negative electricity. Like alkali and acid, these generally mask or neutralise each other's effects, and we only become conscious of their special properties, when abnormal proportions are present.

Apparent electricity and gravitation are the result of absorption of electricity by protons and electrons. Electrostatic intensity is proportional to the rate of change of concentration of apparent electricity.

Magnetic forces are ether currents set up by the spinning motion of electrons and protons.

The properties of Refractive, Dispersive, and Dielectric media depend on the super-position of the motion of cross currents of ether, on ethereal wave-motion that is being propagated through the medium. These cross currents are continually maintained by the atomic magnetic shells.

The polarisation of light is due to the two kinds of reflection—differing by half a wave-length—that occur at surfaces of separation.

The ether permeates both space and atoms, everything in fact except protons and electrons—synthetic compounds from whose surfaces positive and negative electricity are reflected respectively.

Dr. Aston's results may be interpreted as indicating that the restricted absorption of negative electricity, leads to the formation of protons of different masses. Whether some future Millikan will discover among the β particles electrons of variable mass, the sequel must disclose.

All mechanical forces may be ultimately resolved into the rates of change of momenta of four sets of particles—protons, electrons, and the two electricities.

Strain, or the alteration of shape which elastic solids experience when acted upon by outside forces, is the result of the deformation of the normal orbits of the electron shells surrounding the protons of atoms. The mobile equilibrium of these shells is maintained by the magnetic streams of ether which the electron and proton shells maintain, which balance the electric pressure on the protons and electrons.

The shells consist of a small number of similar constituents revolving in common orbits.

Finally it is suggested that electric movements are due to negative (or positive) electricity urging the "charge of electrons" (or protons) on a body in the direction in which the former is least concentrated.

INDEX.

- ABERRATION, 122.
 Absorption, 68.
 Acetylene, 46.
 Acid activation, 36.
 Acridine, 61.
 Activation, 34.
 Active valence, 4, 34, 43.
 Aldehydes, 50.
 Alizarin, 59.
 Alkali metals, 90.
 Allison, S. P., 6, 28.
 α particles, 109.
 Ammonia, 18, 19, 30, 41.
 Anomalous dispersion, 73.
 Anthranilic acid, 47.
 Apparent electricity, 103, 123.
 Armstrong, H. E., 55, 56.
 Aromatic structure, 55, 83, 84.
 Arrhenius, S. A., 27, 91.
 Aston, F. W., 105, 123.
 Atomic association, 16-32, 110.
 — volume, 25, 27.
 Atropine, 28.
 Azo dyes, 57.

 BAEYER, Von, 62.
 Baker, H. B., 51.
 Balmer series, 70.
 Baly, E. C., 60.
 Band spectra, 71.
 Barkla, C. G., 76.
 Basic activation, 36, 39.
 — beryllium acetate, 26.
 Beckmann transformation, 47.
 Becquerel, H., 74.
 Benzene, 55.
 β particles, 124.
 Body colour, 73.

 Bohr, N., 71, 75.
 Bonds, 4, 22, 47, 50, 54.
 — shifting, 49.
 Bone, W. A., 52.
 Boron trimethide, 30.
 Boys, V., 53.
 Bragg, Sir W., 22, 24, 26, 27, 29,
 31, 53, 54, 81.
 Bragg, W. L., 24, 54.

 CANNIZZAROS, 51.
 Carbon, 43, 81.
 — monoxide, 46.
 — tetrachloride, 4.
 Carboxyl, 46, 52.
 Catalysis, 21, 32.
 Cementite, 95.
 Centrifugal force, 25.
 Cerium, 14.
 Chadwick, 27.
 Change of state, 22.
 Chlorine, 38, 67.
 Chromium, 12, 39.
 Chromophores, 57, 86.
 Clark, D., vi.
 Close packing, 97.
 Collapsible shells, 69.
 Coloured cations, 65.
 Colour, 57, 65, 73, 86.
 Complex molecules, 29.
 Compton, A. H., 108.
 — effect, 69, 80.
 Conductors, 81, 88, 89.
 Copper, 52, 65.
 Crystal structure, 20, 22, 24, 26,
 27, 29, 31, 53, 54, 81.
 Currie, 123.
 Cyclic compounds, 55, 83.

- DAMPING effect, 82.
 Deactivation, 34, 85.
 De Broglie, 76.
 De la Rue, W., 23.
 Diamagnetism, 111.
 Diamond, 81.
 Dielectrics, 118.
 Dispersion, 118.
 Dixon, H. B., 52.
 Double bonds, 47, 50, 54.
 EASTMAN, E. D., 35, 47.
 Einstein, 107, 121.
 Electric force, 17, 25, 102, 105.
 Electrode, 98.
 Electron orbits, 3, 22, 49, 69, 79, 80.
 Electrons, 2, 8, 68.
 Electricity, 103, 123.
 Emission, 68, 73.
 Ether, 99-124.
 — absorption, 102.
 Ethylene, 46.
 Ewing, Sir J. A., 95.
 FARADAY, M., 20, 91, 108.
 Fatty acids, 52.
 Ferrocyanides, 31.
 Fluorescence, 74.
 Freezing-points, 22.
 Fresnel, A., 113.
 Fumaric acid, 47.
 Furan, 55.
 GOLD, 40, 96.
 Graphic formulæ, 3, 17-19.
 Graphite, 81.
 Gravitation, 105, 121.
 HAIDINGER, 73.
 Halogens, 66.
 Hardness, 81, 90.
 Hartley, W. N., 60.
 Heat, 110.
 Henrici, 24.
 Heteroalent, 17.
 Heusler's alloys, 95.
 Homovalent, 17.
 Hopkins, B. S., 14.
 Huygens, 113.
 Hydrogenation, 45.
 Hydrogen linkage, 29, 48, 51, 110.
 Hyoscyamine, 28.
 ICE, 29.
 Induced currents, 110.
 Indigo, 64.
 Inert gases, 7, 25.
 Ingold, E. K., 49.
 Insulators, 42, 88.
 Ions, 21, 29, 32, 41, 66, 67, 90, 91, 98.
 Iron, 12, 65, 72, 93.
 Isatin, 47.
 JEANS, J. H., 100.
 Jupiter's satellites, 23.
 KETO-ENOLIC, 48, 60.
 Ketones, 48, 50.
 Kipping, S. P., 24.
 Kopp, H., 28.
 Kossel, 75.
 LATENT valence, 4, 43, 49, 50, 54.
 Le Bel, 23.
 Le Seur, H., 53.
 Levy, 14.
 Lewis, G. N., v, 35.
 Lindh, A. E., 6, 28.
 Linnæus, 2.
 Liquefaction, 22, 110.
 Lodge, Sir O., 100.
 Lyman series, 70.
 MAGNETISM, 20, 49, 93, 108, 123.
 Manganese, 12, 39, 43.
 Maleic acid, 47.
 Mass, 105.
 Maxwell, J. C., 23, 112.
 McLennan, J. C., 96.
 Mechanical force, 124.
 Mercury, 31, 98.
 Metallic structure, 6, 25, 91, 93, 94, 97.
 Methane, 18, 46.
 Michelson, A. A., 121.

- Migrating electrons, 57, 72, 81, 88, 89.
 Millikan, A., 124.
 Morgan, G. T., 26, 27.
 Moseley, H. G. J., 2, 76.
- NAPHTHALENE, 56.
 Nernst, W., 98.
 Newton, Sir I., 99, 107, 113, 115, 119.
 Nickel, 26.
 Nitric acid, 46, 75.
 — oxide, 46.
 Nitrobenzene, 58.
 Nitrogen peroxide, 46, 58.
 — 35, 43, 46.
 Noyes, W. A., 67, 92.
 Nucleus, 104, 109.
- OPTICAL activity, 23, 24, 28, 45.
 Orbits of electrons, 3, 22, 49, 69, 79, 80.
 Osmium, 26, 77.
 Ostwald, W., 28.
 Oxidation, 1, 33, 43, 47.
 Oxygen, 35.
- PALLADIUM, 13, 24.
 Para changes, 55.
 Parson, 108.
 Paschen series, 70.
 Peachey, S., 45.
 Perchlorates, 19.
 Periodic sub-groups, 7.
 — system, 7, 11-14.
 Perkin, Sir W., 20, 51.
 Permanganates, 39, 43, 60, 73.
 Phosphorescence, 74.
 Phosphorus, 38, 41.
 — pentoxide, 16.
 Photoelectric activity, 92, 119.
 Pickering, S. V., 53.
 Platinum, 13, 24, 31.
 Polarisation, 20, 73, 89, 114.
 Polyphenyl, 83.
 Pope, Sir W., 23, 28, 45.
 Potential valence, 3, 5, 33, 43, 47, 81, 88.
- Prevost, 106.
 Propiolic acid, 47.
 Protons, 105, 123.
 Pyridine, 55.
 Pyrrole, 55.
- QUARTETS, 6, 40.
 Quartz, 18, 24, 31.
 Quinones, 54, 59.
- RADIAL electrons, 3, 6, 40.
 Radiation, 111.
 Rare earths, 14, 15, 66, 77, 109.
 Reduction, 33, 43, 85.
 Reflection, 73, 89, 110, 114.
 Refraction, 117.
 Relativity, 121.
 Röntgen, W. C., 123.
 Rosaniline, 62.
 Ruthenium, 19, 26, 77.
 Rutherford, Sir E., 2, 27, 113, 123.
- SELENIUM, 85.
 Siegbahn, M., 76, 77.
 Silicon, 24.
 Silicofluorides, 31.
 Soap, 53.
 Solidification, 22, 110.
 Spinning, 79, 108.
 Spiral motion, 70, 79, 108, 109.
 Stark, J., 69.
 Steric hindrance, 27.
 Stewart, A. W., 60.
 Stokes, Sir G. G., 73.
 Strained metals, 96.
 Sulphur, 24, 37, 43.
 Symmetry, 23-32.
- TAUTOMERIC change, 47, 48, 57, 60.
 Temperature, 87.
 Thiele, J., 49.
 Thiophene, 55.
 Thompson, Sir J. J., 103, 113, 123.
 Thorpe, Sir T. E., 28.
 Tin, 3, 24.

- | | |
|--------------------------------------|-------------------------|
| Transition elements, 12. | WATER, 18. |
| Transverse vibrations, 101, 112. | Werner, A., 24. |
| Triphenyl methyl, 63. | Wetting, 21. |
| Triple bonds, 47, 50. | Wislicenus, W., 48. |
| Tutton, A. E., 28. | |
| Tyndall, J., 107. | X-RAYS, 24, 28, 69, 75. |
| | |
| VALENCE electrons, 3, 4, 34, 36, 39, | YOUNG, J. F. T., 95. |
| 43, 49, 50, 54. | — T., 113. |
| Van't Hoff, J. H., 23. | |
| Volatile compounds, 26. | ZEEMAN, P., 69. |



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